

# **Detecting dissolved PAHs from oil spills using passive samplers in cold water and ice cores**

**A Progress Report Submitted to  
The Coastal Response Research Center**

**Submitted by**

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**Reporting Period: April 15, 2009 to December 15, 2009 (Final Report)**

**Submission Date: October 25, 2010**



This project was funded by a grant from NOAA/UNH Coastal Response Research Center.  
NOAA Grant Number(s): NA04NOS4190063. Project Number: 08-102



## Abstract

Passive samplers have been demonstrated to accumulate hydrophobic organic compounds proportional to the dissolved concentration present in the surrounding water column. The accumulated concentration in the passive samplers can be converted into the dissolved concentration by using equilibrium partitioning coefficients ( $K_{PS-W}$ ) at a specific temperature and salinity. In this study, the  $K_{PS-W}$  between water and two passive samplers, polyethylene (PE) sheets and solid-phase micro-extraction (SPME) fibers, were derived theoretically for a suite of polycyclic aromatic hydrocarbons (PAHs), and then verified experimentally at the extreme temperatures and hyper-saline conditions similar to those found in the Arctic. In subsequent studies, the experimentally derived  $K_{PS-W}$  values were utilized to derive water concentrations in a simulated oil spill and a field deployment in Narragansett Bay. Both the SPMEs and PEs were reliable options to determine water concentrations during an oil spill, while PEs appear to be a more valuable tool at consistently capturing background concentrations of PAHs present in the environment. The passive samplers, with the verified  $K_{PS-W}$  values, can be used to better understand the fate and transport of PAHs in the natural waters including those found in the Arctic environment.

**Keywords:** PAHs, passive samplers, equilibrium partitioning coefficients, temperature, salinity

## Acknowledgements

I would like to thank Rainer Lohmann, my advisor, who took me on as his student. I was not the conventional student and I would like to thank him especially for his patience, understanding, and guidance over the past four years. Rainer has taught me much along the way, both inside and outside the laboratory, and introduced me to Josh and the world of passive sampling. My success in the future is in part to Rainer.

I would also like to thank to my fellow Lohmann lab mates. Without their support, I am sure I would have gray hair by now. Carey Friedman was always there with wise words and a reassuring smile, and I would like to thank her for introducing me to NPR, as well as analyzing my water samples for DOC content. Lin Zhang saved the day many a time on the GC/MS with his magic computer skills. Matthew Lambert, aka “Muscles”, was always there to lend a hand and a smile when I needed one. Victoria Sacks, my lab sista, kept me company on many a late night in the lab and the office, sharing popcorn and stories. Julia Sullivan, with her quiet ways and large heart, was my partner in crime in the lab and served as my extra pair of hands whenever I needed her. Dave Adelman provided the engineering for this work; if something was broken or not working, Dave could fix it and if possible improve it. The newbie’s in the lab, Shifra Yonis and Kari Pohl, were always ready to learn, and excited about it.

Many others have contributed to this work in one way or other. Victoria Dekany, a SURFO at URI-GSO, provided PRC research over her summer at GSO and her data assisted me in determining the correct PRCs to use for my research. Rob Burgess kindly donated his expertise and stir plates to assist in the completion of this work. Mark Cantwell was always there to assist with GC/MS problems, and saved me days quantifying my data. I would like to thank Ed Baker and the Champlin Foundation for the use of the environmental chambers. The Robinson and Moran labs allowed me to borrow equipment and Milli-Q when I was in need.

I would like to thank my committee members, Jim Quinn, Vinka Craver, Rob Burgess, and Anne Veeger for their interest, willingness, and guidance.

I would like to give many thanks to the NOAA/UNH Coastal Research Response Center (Grant number NA04NOS4190063) for their financial support of this work in search of the fate and transport of oil in ice.

## Table of Contents

1.0	Introduction.....	1
2.0	Objectives .....	4
3.0	Methods.....	4
4.0	Results.....	17
5.0	Discussion of Importance to Oil Spill Response/Restoration.....	53
6.0	Technology Transfer.....	53
7.0	Achievement and Dissemination .....	56
	References.....	57
	Appendix.....	60

## List of Tables

<b>Table 1.</b> PAHs investigated in this study .....	6
<b>Table 2.</b> Deuterated compounds utilized as PRCs in this study.....	7
<b>Table 3.</b> Deuterated compounds employed as internal surrogates and injection standards .....	7
<b>Table 4.</b> PAHs contained in NIST standard reference material® 2260a and their corresponding concentrations .....	8
<b>Table 5.</b> Various temperatures and corresponding salinities of equilibrium partitioning experiments .....	11
<b>Table 6.</b> List of the priority PAHs and LMW compounds present in the Statfjord crude oil with their respective log $K_{OW}$ values and molecular weight.....	26
<b>Table 7.</b> Composition of PAHs in the WSF of Statfjord crude oil .....	45
<b>Table 8.</b> List of experimental log $K_{SPME-W}$ values determined in this study for the priority PAHs and LMW compounds present in the Statfjord crude oil.....	54
<b>Table 9.</b> List of experimental log $K_{PE-W}$ values determined in this study for the priority PAHs and LMW compounds present in the Statfjord crude oil.....	55

## List of Figures

<b>Figure 1.</b>	Metal rack constructed from stainless steel wire and screening to assist SPMEs to reach equilibration with PRCs. ....	10
<b>Figure 2.</b>	Laboratory set up to verify SPME loss rate incorporating an Erlenmeyer flask attached to a laboratory faucet to simulate turbulent conditions in the field .....	10
<b>Figure 3.</b>	Freezer arrangement incorporating a shaker table to hold the SPME samples and a stir plate for the PE samples to complete the -15 °C experiment. ....	12
<b>Figure 4.</b>	PEs threaded on stainless steel wire (A) and attached to deployment line (B) for the field deployment in Narragansett Bay. ....	15
<b>Figure 5.</b>	Copper housing manufactured to house SPMEs during the field deployment (A) and copper housing attached to deployment line with stainless steel wire for the field deployment in Narragansett Bay .....	16
<b>Figure 6.</b>	Active sampling arrangement with PUFs inserted in the tall cylinder (left) and filters placed in the flat platform (right) to collect dissolved PAH concentrations present in Narragansett Bay .....	17
<b>Figure 7.</b>	NIST standard concentration compared to the PAH laboratory curve derived concentration. Only PAHs present in the laboratory standard are displayed in the figure .....	18
<b>Figure 8.</b>	Average PRCs concentrations of seven separate SPME batches of with relative standard deviations less than 25% .....	20
<b>Figure 9.</b>	Percent lost of PRCs by SPMEs during laboratory loss rate experiment mimicking turbulent conditions in the field .....	21
<b>Figure 10.</b>	Averaged experimentally derived $K_{SPME-W}$ at 20 °C and salinities of 0 and 35 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.....	25
<b>Figure 11.</b>	Averaged experimental $K_{SPME-W}$ at 20 °C and salinities of 0 and 35 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil .	27
<b>Figure 12.</b>	Averaged experimentally derived $K_{PE-W}$ at 20 °C and salinities of 0 and 35 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.....	28
<b>Figure 13.</b>	Averaged experimental $K_{PE-W}$ at 20 °C and salinities of 0 and 35 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil .	29

## List of Figures (continued)

<b>Figure 14.</b>	Averaged experimentally derived $K_{SPME-W}$ at 2 °C and salinities of 0 and 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.....	30
<b>Figure 15.</b>	Averaged experimentally derived $K_{PE-W}$ at 2 °C and salinities of 0 and 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.....	31
<b>Figure 16.</b>	Averaged experimental $K_{SPME-W}$ at 2 °C and salinities of 0 and 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. 33	
<b>Figure 17.</b>	Averaged experimental $K_{PE-W}$ at 2 °C and salinities of 0 and 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil .34	
<b>Figure 18.</b>	Averaged experimentally derived $K_{SPME}$ and $K_{PE-W}$ at -4 °C and salinity 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.....	35
<b>Figure 19.</b>	Averaged experimental $K_{SPME-W}$ and $K_{PE-W}$ at -4 °C and a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil .....	36
<b>Figure 20.</b>	Averaged experimentally derived $K_{SPME}$ and $K_{PE-W}$ at -15 °C and a salinity 245 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations .....	38
<b>Figure 21.</b>	Averaged experimental $K_{SPME-W}$ and $K_{PE-W}$ at -15 °C and a salinity of 245 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil .....	39
<b>Figure 22.</b>	Averaged experimental $K_{SPME-W}$ at a salinity of 0 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature .....	40
<b>Figure 23.</b>	Averaged experimental $K_{PE-W}$ at a salinity of 0 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature .....	41
<b>Figure 24.</b>	Averaged experimental $K_{SPME-W}$ at a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature.....	43
<b>Figure 25.</b>	Averaged experimental $K_{PE-W}$ at a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature .....	44

**List of Figures (continued)**

**Figure 26.** Averaged water concentrations from liquid-liquid extraction of Statfjord water samples compared to SPME and PE derived water concentrations a few LMW PAH compounds .....47

**Figure 27.** Averaged water concentrations from liquid-liquid extraction of Statfjord water samples compared to SPME and PE derived water concentrations a few LMW PAH compounds .....48

**Figure 28.** Averaged water concentrations from active sampling of Narragansett Bay compared to SPME and PE derived water concentrations a few LMW PAH compounds .....50

**Figure 29.** Averaged water concentrations from active sampling of Narragansett Bay compared to SPME and PE derived water concentrations a few LMW PAH compounds .....51

## 1.0 Introduction

With the decreasing extent of the polar ice caps as a result of global climate change as well as advances in technology, anthropogenic activity in the Arctic region is projected to increase (Raineault & Sher 2009). Internationally, there is an interest in expanding vessel traffic as well as the exploration of oil and gas reserves in the Arctic (Raineault & Sher 2009), all of which increase the likelihood of a release of oil and gas and their constituents (i.e., polycyclic aromatic hydrocarbons) into the environment; hence there is an urgent need to better understand the impact of anthropogenic activities, specifically oil spills, to this unique environment.

An example of the effects of increased anthropogenic activities in the Arctic is the increased potential for oil spills. When oil is spilled into the Arctic environment, it can become frozen and trapped in the ice sheet. The ice can be pushed by currents to a new environment and melt, potentially further extending the toxic effects of the oil (Faksness 2008). Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic compounds and are amongst the most toxic compounds present in oil (Singer et al. 2000). As salt water freezes, the water molecules arrange into a crystalline formation, which forces the salt molecules out forming a hypersaline or brine solution between the crystals. The brine then forms channels in the ice. These brine channels are thought to transport PAHs through the ice. Some studies suggest that there is a downward migration of dissolved PAHs through brine channels (Faksness & Brandvik 2005). In contrast, Otsuka et al. (2004) reported an upward migration of bulk oil in brine channels during melting. Further investigation into the fate and transport of these compounds is necessary to evaluate the environmental risk of PAHs in the arctic environment.

Passive samplers have been proven to accumulate compounds, such as PAHs, in proportion to the dissolved concentration of the compound present in the aquatic environment (Mayer et al 2003). Passive samplers are a useful alternative to conventional direct measurement of environmental phases (i.e. liquid-liquid extraction), such as water and sediment, for studies completed to derive bioaccumulation and bioavailability. When passive samplers are deployed to measure PAHs in the water column, only the dissolved or bioavailable fraction present in the water column is accumulated (Mayer et al 2003). In sediments, passive samplers reflect the concentration of contaminants dissolved in the water present within the sediment, also called porewater (Friedman et al. 2009). It is the concentration of compounds in the porewater that most closely reflects their bioavailability and concentration in benthic organisms (Friedman et al. 2009; Tomaszewska & Luthy 2008). PAHs sorbed to particles or colloids in the water column or in sediments are no longer bioavailable and are difficult to separate from the truly dissolved and bioavailable PAHs (Namiesnik et al. 2005). Thus, when water is sampled for PAHs using conventional methods, the dissolved concentrations are often overestimated due to the inclusion of PAHs associated with colloids. Passive samplers are also a preferred method for measuring PAHs for their ease of sampling, lower detection limits in the field, and minimization of contaminated blanks (Namiesnick et al. 2005). Passive samplers can often be an inexpensive and reliable option compared to conventional methods (Namiesnick et al. 2005).

As stated above, passive samplers take up compounds in proportion to the dissolved concentration present in the environment until equilibrium between the passive sampler and the dissolved concentration is reached. Until equilibrium is reached, the passive samplers reflect a time averaged concentration. If the sampler is deployed longer than needed for equilibrium to be

reached, the results will reflect the more recent exposure. Conventional methods of water analysis take samples at a discrete point in time, representing the concentration only at that time. Depending on the circumstances of the sample collection, such as currents, changing tides, losses to the atmosphere, or other environmental factors, the discrete sample is not an accurate representation of the overall concentrations in the environment. The time averaged concentration determined from passive sampling is a more appropriate reflection of the longer-term exposure in the environment.

Though passive samplers are an excellent option for assessing dissolved PAH concentrations, their performance has not been tested under the harsh conditions of the Arctic environment. Polyethylene samplers (PEs) and solid phase micro-extraction (SPMEs) fibers, which are optical fiber with a poly(dimethylsiloxane) coating, are two types of passive samplers that have been proven effective at assessing environmental concentrations of organic pollutants (Adams et al. 2007; Cornelissen et al. 2008). When used in the water column, a passive sampler (PS) takes up organic pollutants until equilibrium is reached between the two phases, the passive sampler as one phase, and the water column as another. Equilibrium is defined as the distribution of a chemical in two phases as governed by the free energy for this process. At equilibrium, no net change in concentration between the phases occurs over time. Equilibrium partitioning coefficients are used to represent this relationship. Equilibrium partition coefficients ( $K_{PS-W}$ ) are generally determined in the laboratory under standard conditions and are used to relate the passive sampler concentration ( $C_{PS}$ ) to the dissolved concentration in the water column ( $C_W$ ; equation 1).

$$K_{PS-W} = \frac{C_{PS}}{C_W} \quad (1)$$

$K_{PS-W}$  is the ratio of the concentration of the compound in the passive sampler (e.g., ng/ $\mu$ L) over the concentration of the compound in the water (e.g., ng/ $\mu$ L) under standard conditions. If the  $K_{PS-W}$  is known for a compound and a PS is deployed in the environment, the concentration of the water (i.e., dissolved) can then be calculated as:

$$C_W = \frac{C_{PS}}{K_{PS-W}} \quad (2)$$

When samplers are deployed in the environment, it may take an extended period of time for equilibrium to be reached. To assist in evaluating the extent of equilibrium reached by the compounds of interest in the sampler during field deployment and to allow the use of shorter deployment periods, performance reference compounds (PRCs) may be applied (Booij et al 2002). PRCs are compounds that are chemically similar to the compounds of interest, but are unlikely to occur in the environment. For example, carbon labeled or deuterated molecules (PAHs) can serve as PRCs. PRCs are impregnated at a known concentration in the passive sampler prior to deployment. By determining the concentration of PRCs along with the contaminants of interest in the passive sampler after recovery, the extent of equilibrium reached can be determined through the calculation of a loss rate,  $k_e$  (equation 3):

$$k_e = -\ln \left( \frac{C_{PRC(0)}}{C_{PRC(t)}} \right) t^{-1} \quad (3)$$

where  $C^0$  is the concentration of a PRCs at time zero and  $C^t$  is the concentration after  $t$  time of the deployment. Since there is only a loss of these compounds from the passive sampler, their loss rate is assumed to be similar to the uptake of the compounds of interest (Adams et al 2007). Thus, PRCs can be employed to infer the extent of equilibrium of the compounds of interest reached after a given deployment duration. The loss rate ( $k_e$ ) tends to decline with increasing molecular weight and increasing  $\log K_{PS-W}$  and can be calculated through assessing the concentrations of the PRCs at time zero and after exposure time, as seen in equation 5. Concentrations of the PRCs can be evaluated at the various sampling intervals and the  $k_e$  and % lost can be determined:

$$\% \text{ lost} = \left[ 1 - \left( \frac{C_{PRC(t)}}{C_{PRC(0)}} \right) \right] \times 100 \quad (4)$$

The percent loss can be calculated to predict the times necessary for other PAHs to reach 95% equilibrium in the field under turbulent conditions. If conditions in the field were not turbulent and samplers did not reach equilibrium, then PRCs can be used to correct for non-equilibrium. If  $k_e$ ,  $K_{PS-W}$ , the concentration in the passive sampler ( $C_{PS}$ ) and time ( $t$ ) are known, then  $C_W$  at equilibrium will be:

$$C_W = \frac{C_{PS}}{(1 - e^{-k_e * t}) K_{PS-W}} \quad (5)$$

As noted above, the  $K_{PS-W}$  is usually experimentally determined at standard temperatures (20 - 25 °C) and zero salinity. It has been shown that there is a temperature and salinity effect on the  $K_{PS-W}$  (Adams et al 2007), so it needs to be adjusted to address the varying conditions present in the environment where the passive samplers are deployed (Schwarzenbach et al. 2003). As the temperature of the environment decreases, as it does in the Arctic environment, the partitioning of the compound into the passive sampler increases due to decreased solubility (Schwarzenbach et al. 2003). Due to the lower solubility in the water column and their high hydrophobicity, it is more energetically favorable for the compounds to partition into the passive sampler. As the salinity of the environment increases, as seen in brine channels in the Arctic, the compounds are less soluble and “salting out” occurs increasing the partitioning of the compound into the passive sampler (Schwarzenbach et al. 2003). Again, with the higher salt content and the decreased solubility, it is more energetically favorable for the compounds to partition into the passive sampler, therefore increasing the  $K_{PS-W}$ .

The effects of temperature and salinity on the  $K_{PS-W}$  can be calculated using the van't Hoff (equation 6) and Setschenow equations (equation 7), respectively (Schwarzenbach et al. 2003). The van't Hoff equation uses the compound's enthalpy of phase change ( $\Delta H$ ; kJ/mol), the gas constant ( $R$ ; kJ/mol-K), the temperature  $K_{PS-W}$  was originally determined at  $T_o$ , and the temperature that the  $K_{PS-W}$  is desired at  $T$ :

$$K_{PS-W}(T_1) = K_{PS-W}(T_2) \exp \left[ \frac{-\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right] \quad (6)$$

The Setschenow equation modifies the  $K_{PS-W}$  at a salinity of zero and adjusts it utilizing the empirical Setschenow constant ( $K_S$ ) and the molar concentration of salt, [salt], present in the water, as shown below:

$$K_{PS-W}(salt) = K_{PS-W}(0) \times 10^{+K_S*[salt]} \quad (7)$$

Both of these equations have been proven reliable at moderate temperatures (30°C to 2°C; Adams et al. 2007) and salinities (0 to 36.7 psu; Xie et al. 1997). Yet,  $K_{PS-W}$  for SPMEs and PEs have not been validated at low temperatures and hyper-saline conditions, as those found in the Arctic ice sheet (as low as -40°C) and brine channels (exceeding 100 psu; Thomas & Dieckman 2003). For passive samplers to be reliably utilized in the unique environment of the Arctic to investigate the fate and transport of oil, the temperature and salinity effects on the equilibrium partitioning coefficients need to be validated.

## 2.0 Objectives

In this study, the equilibrium partitioning coefficient between PEs and water ( $K_{PE-W}$ ) and SPMEs and water ( $K_{SPME-W}$ ) at various salinities and temperatures were calculated and compared to the experimental values obtained under controlled or standard laboratory conditions. Once these equilibrium partitioning coefficients are verified under Arctic-like conditions, these passive samplers will be valuable tools to assess the behavior of PAHs under these unique conditions. To test this premise, a mock oil spill was created in the laboratory to evaluate the effectiveness of the passive samplers. The passive samplers were also deployed in Narragansett Bay in March to assess the hardiness of the passive samplers during a cold water field deployment. In the event an oil spill should occur, which unfortunately is inevitable with the increase of vessel traffic and oil exploration in the Arctic, passive samplers can be deployed to track PAH concentrations throughout the affected area to help in damage assessment and to assist in remediation efforts.

## 3.0 Methods

*Overview.* This research was composed of multiple steps conducted in both the laboratory and the field. First, PAH solutions to be investigated were prepared. The passive samplers were then impregnated with performance reference compounds (PRCs). After that, passive samplers were exposed to water enriched with PAHs and allowed to equilibrate at various temperatures and salinities to derive the  $K_{PS-W}$  values. These experimental  $K_{PS-W}$  values were then compared to theoretically derived values obtained through the van't Hoff and Setschenow equations (equations 5 & 6). To evaluate these results, another laboratory experiment was conducted to simulate oil spill conditions using crude oil. Finally, the passive samplers were deployed in cold water conditions in Narragansett Bay to verify their hardiness and usefulness under field conditions.

*Targeted oil compounds.* Since the overall focus of this research was to investigate the fate and transport of oil in ice, 53 native PAHs that are commonly present in oil were identified and used

to prepare a laboratory standard curve ranging from lower molecular weight components (e.g., naphthalene) to compounds of higher molecular weight (e.g., chrysene and benzo(a)pyrene) (Table 1). Additionally, three deuterated compounds were utilized as PRCs (Table 2). Different deuterated PAHs were also used as internal surrogates and injection standards (Table 3). All native compounds and PRCs were precisely measured into a PAH mixture at a known concentration. This solution was combined with internal surrogates and injection standard to generate a six point laboratory standard curve with varying concentrations. Native PAH concentrations, PRCs and injection standard concentration varied in each point of the curve, while the internal surrogate concentration was kept constant. This allowed for proper quantification of concentration of samples on the gas chromatogram/mass spectra (GC-MS).

*NIST Standard Calibration.* A National Institute of Standards and Technology (NIST) PAH standard was purchased to calibrate the PAH standard curve used to analyze all samples prepared. NIST standard reference material (SRM) 2260a is a solution in toluene containing 36 aromatic hydrocarbons and primary PAHs (Table 4). Eighteen of the PAHs were present in the laboratory standard curve (Table 4). The NIST sample was not altered prior to analysis and 100  $\mu\text{L}$  was added directly to an insert vial along with laboratory internal surrogates and injection standard. The NIST standard was analyzed in duplicate and the concentrations averaged to compare to the laboratory standard concentrations. This was completed once to validate the standard curve concentrations.

*Passive samplers.* For all experiments, polyethylene, 25  $\mu\text{m}$  in thickness, manufactured by a commercial sheeting company (Carlisle Plastics, Inc., Minneapolis, MN, USA) was purchased from a local hardware store. SPME fibers were acquired from Polymicro Technologies, LLC, (Phoenix, AZ, USA) with a poly(dimethylsiloxane) coating thickness of 50  $\mu\text{m}$  and a total diameter of 160  $\mu\text{m}$ . Passive samplers were pre-cleaned in solvents twice, PEs in dichloromethane (DCM) and SPMEs in methanol, prior to use. For the laboratory portion of the study, PEs were cut into small pieces with a mass of approximately 0.09 mg (ca. 1  $\text{cm}^2$ ). For the field deployment, PEs were cut into sheets of approximately 1.5 g (ca. 15 cm long by 5 cm wide). SPMEs were cut into 10 cm sections and utilized in both the laboratory and field experiments. Once samplers were retrieved from the various experiments, they were extracted in hexane and internal surrogates added at the time of extraction. The extracts were then concentrated under a flow of nitrogen gas. Injection standard (external standard) was added prior to analysis with gas chromatography/mass spectrometry (GC/MS) (Agilent, Santa Clara, CA, USA) and quantified using ChemStation software.

Concentrations of PAHs and PRCs in both passive samplers were normalized to the weight (PE) and volume (SPME) of the passive sampler utilized. PEs were weighted on an analytical balance, while the SPME volume was determined by the length of SPME utilized multiplied by the PDMS coating dimensions determined by the manufacturer.

*Instrument Analyses.* All samples were analyzed for PAHs on an Agilent 6800 CG coupled to an Agilent 5973N MS operated in the negative electronic ionization mode. The GC/MS was operated in splitless mode with an Agilent J&W DB-5MS column (30 m, internal diameter 250  $\mu\text{m}$ ) installed for the majority of the samples. A sample volume of 1  $\mu\text{L}$  was injected via autosampler into the injection port, which was maintained at 275  $^{\circ}\text{C}$  and the MS transfer line at 280  $^{\circ}\text{C}$ . The column flow was held constant at 2  $\text{mL min}^{-1}$ . The temperature program for all

**Table 1.** PAHs investigated in this study

Compounds of Interest	Molecular Weight
Phenol	94
m-Cresol	108
p-Cresol	108
o-Cresol	108
2,3-Dimethyl phenol	122
3,4-Dimethyl phenol	122
p-Ethyl phenol	122
m-Ethyl phenol	122
o-Ethyl phenol	122
Naphthalene	128
2,3,5-Trimethyl phenol	136
2,4,6-Trimethyl phenol	136
2-Methyl naphthalene	142
2,3,5,6-Tetramethyl phenol	150
Acenaphthylene	152
Acenaphthene	154
Biphenyl	154
1,5-Dimethyl naphthalene	156
Fluorene	166
2,3,5-Trimethyl naphthalene	170
2-isopropyl naphthalene	170
Phenanthrene	178
Anthracene	178
2-Methyl fluorene	180
1,4,6,7-Tetramethyl naphthalene	184
1,2,5,6-Tetramethyl naphthalene	184
Dibenzothiophene	184
4,5-Methylene phenanthrene	190
1-Methyl phenanthrene	192
9-Methyl anthracene	192
9-Ethyl fluorene	194
2-Methyl Dibenzothiophene	198
Pyrene	202
Fluoranthene	202
3,6-Dimethyl phenanthrene	208
9-n-Propyl fluorene	208
1,2-Dimethyl dibenzothiophene	212
2,6-Diisopropyl naphthalene	212
1-Methyl pyrene	216
1,2,5/1,2,7-Trimethyl phenanthrene	220
2,4,7-Trimethyl dibenzothiophene	226
Chrysene	228
Benz(a)anthracene	228
Retene	234
1-Methyl chrysene	242
Benzo[a]pyrene	252
Perylene	252
Benzo(b)fluoranthene	252
Benzo(h)fluoranthene	252
7,12-Dimethyl benz(a)anthracene	256
Benzo(g,h,i)perylene	276
Indeno(1,2,3-c,d)pyrene	276
Dibenzo(a,h)anthracene	278

**Table 2.** Deuterated compounds utilized as PRCs in this study

<b>Performance Reference Compounds</b>	<b>Molecular Weight</b>
Naphthalene-d <sub>8</sub>	136
Pyrene-d <sub>10</sub>	212
Benzo[a]pyrene-d <sub>12</sub>	264

**Table 3.** Deuterated compounds employed as internal surrogates and injection standards

<b>Internal Surrogates</b>	<b>Molecular Weight</b>
Acenaphthene-d <sub>10</sub>	164
Phenanthrene-d <sub>10</sub>	188
Chrysene-d <sub>12</sub>	240
Perylene-d <sub>12</sub>	264
<b>Injection Standard</b>	<b>Molecular Weight</b>
p-terphenyl-d <sub>14</sub>	244

**Table 4.** PAHs contained in NIST standard reference material® 2260a and their corresponding concentrations

<b>Compound</b>	<b>Concentration (µg/mL)</b>
Naphthalene	9.89 ± 0.26
Biphenyl	4.85 ± 0.12
Acenaphthylene	5.41 ± 0.17
Acenaphthene	4.80 ± 0.11
Fluorene	4.07 ± 0.10
Dibenzothiophene	3.80 ± 0.15
Phenanthrene	10.01 ± 0.10
Anthracene	3.231 ± 0.047
4 <i>H</i> -Cyclopenta[ <i>def</i> ]phenanthrene	2.01 ± 0.10
Fluoranthene	7.200 ± 0.075
Pyrene	7.741 ± 0.072
Benzo[ <i>ghi</i> ]fluoranthene	2.953 ± 0.039
Cyclopenta[ <i>cd</i> ]pyrene	1.694 ± 0.021
Benzo[ <i>c</i> ]phenanthrene	3.986 ± 0.031
Benzo[ <i>a</i> ]anthracene	3.819 ± 0.067
Chrysene	4.00 ± 0.10
Triphenylene	3.56 ± 0.14
Benzo[ <i>b</i> ]fluoranthene	6.80 ± 0.09
Benzo[ <i>j</i> ]fluoranthene	3.585 ± 0.084
Benzo[ <i>k</i> ]fluoranthene	2.979 ± 0.031
Benzo[ <i>a</i> ]fluoranthene	1.971 ± 0.055
Benzo[ <i>a</i> ]pyrene	3.945 ± 0.047
Benzo[ <i>e</i> ]pyrene	4.07 ± 0.15
Perylene	3.83 ± 0.039
Indeno[1,2,3- <i>cd</i> ]pyrene	3.828 ± 0.026
Benzo[ <i>ghi</i> ]perylene	4.904 ± 0.060
Dibenzo[ <i>a,h</i> ]anthracene	3.940 ± 0.054
Dibenzo[ <i>a,c</i> ]anthracene	2.519 ± 0.022
Dibenzo[ <i>a,j</i> ]anthracene	3.926 ± 0.054
Picene	2.817 ± 0.041
Benzo[ <i>b</i> ]chrysene	3.540 ± 0.029
Anthanthrene	1.907 ± 0.025
Coronene	1.951 ± 0.029
Dibenzo[ <i>a,h</i> ]pyrene	2.518 ± 0.082
Dibenzo[ <i>b,k</i> ]fluoranthene	1.424 ± 0.059
Dibenzo[ <i>a,e</i> ]pyrene	1.970 ± 0.020

samples was as follows: hold 60 °C for 3 min, increased to 110 °C at 5 °C min<sup>-1</sup> and held at temperature for 2 min, increased to 200 °C at 8 °C min<sup>-1</sup>, and finally increased to 315 °C at 5 °C min<sup>-1</sup> and held for 5 min. The total method run-time was 54.25 min.

All samples were analyzed in the selected ion monitoring (SIM) mode on the MS. The ratio of the two most abundant ions, and for some compounds other characteristic ions, were monitored for each compound investigated. PAHs were identified by retention time and confirmed through the compounds mass spectra. Quantification was determined through a 6-point calibration curve which included the native PAHs, PRCs, internal standards and injection standard (Tables 1-3). The calibration curve was run with each set of samples (approximately 30 – 40 samples per set) and one point of the curve was re-run every 10 samples. The detection limit of the calibration curve was 10 pg μL<sup>-1</sup>.

*Performance Reference Compounds.* The first step in the laboratory research was to reproducibly enrich the passive samplers with PRCs. Methods to accomplish this were modified from Booij et al. (2002) for the PEs and ter Laak et al. (2008) for the SPME fibers. More specifically, a solution of 80% pure water (18.2 MΩ cm<sup>-1</sup> Milli-Q<sup>®</sup> filtered water) and 20% methanol was prepared. PRCs were then added at various concentrations and the solution stirred prior to including passive samplers. A metal rack made out of fiberglass screen and stainless steel wire was fabricated in which the SPME fibers were placed to protect and separate them while on the shaker table, thereby allowing more surface area exposed to the PRC solution (Figure 1). Flasks with SPME fibers were placed on a shaker table, while flasks with PEs were stirred until equilibrium was achieved with the PRCs. Once PRC concentrations within the passive samplers were within an acceptable range of each other ( $\pm 10\%$ ) the next step was to assess the loss rate,  $k_e$ , of the PRCs. The loss rate was determined by measuring the PRC concentration in the passive sampler prior to deployment and again after recovery (equation 3). Loss rates had already been investigated for similar PRCs in PEs (unpublished data, Dekany 2007), so only SPME loss rates were evaluated for this research. The PRC concentration in the SPMEs was determined prior to the experiment (time = 0) by GC/MS. SPME loss rate investigations were conducted in the laboratory under turbulent flow condition (1 L/minute). Tap water entered the top of an Erlenmeyer filter flask, flowed over the SPMEs then left out the side vent where the flow was verified (Figure 2). Once flow was verified, sampling time began and the flask was covered in aluminum foil to prevent sunlight penetration. SPMEs were removed in triplicate at the following sampling intervals: 1, 2, 4, 8, 12, 16, 24, 36, 60, and 108 hours. SPMEs were extracted as previously mentioned and loss rates determined as in equation 4 for each PRC.

*Equilibrium partition coefficients.* Equilibrium partition coefficients were determined in the laboratory for various PAHs (Table 1). In climate controlled rooms, tests were performed to cover the range of temperatures and salinities commonly found in the marine environment, especially conditions present in the Arctic environment (Thomas & Dieckman 2003; Table 5). Water samples were prepared at various salinities (245, 100 and 35 psu) using pure water (18.2 MΩ cm<sup>-1</sup> Milli-Q<sup>®</sup> filtered water) and Instant Ocean<sup>®</sup> or Sigma-Aldrich salt mixture, which both mimic the composition of natural seawater. Instant Ocean<sup>®</sup> was used to prepare the water in the -4 °C and 2 °C experiments. The Sigma-Aldrich salt mixture was employed for the 20 °C and -15 °C experiments. The salt mixture was altered between experiments because the Sigma-Aldrich salt mixture was reported by collaborators to more readily dissolve at higher salinities.



**Figure 1.** Metal rack constructed from stainless steel wire and screening to assist SPMEs to reach equilibration with PRCs.



**Figure 2.** Laboratory set up to verify SPME loss rate incorporating an Erlenmeyer flask attached to a laboratory faucet to simulate turbulent conditions in the field.

**Table 5.** Various temperatures and corresponding salinities of equilibrium partitioning experiments

Temperature (°C)	Salinity (psu)
20	0
20	35
2	0
2	100
-4	100
-15	245

To ensure modifying the salt would not affect the results, the composition of the two salt mixtures was compared. Manufacturer tables describing the compositions showed the only difference between the mixtures were in the ancillary ingredients, not the major components in the mixtures. The salt water solutions were prepared in 4 L batches and a rough salinity measurement of each batch verified with a refractometer. A more precise salinity value was obtained through titrations with silver nitrate (Grasshoff 1983). PEs and SPMEs were prepared in triplicate along with a blank and placed in 1L pre-cleaned amber jars filled with water of the various salinities. The triplicate samples were then spiked with a mixture of the 53 oil components (Table 1). To facilitate faster equilibrium times, flasks with PEs were stirred and SPMEs were placed on a shaker table. SPMEs were not stirred due to possible damage to the sampler. These conditions would mimic a very turbulent situation in the natural environment. If the samplers were not agitated in this method, it would take a much longer time period to reach equilibrium.

The equilibrium partition coefficient experiments took place in a climate controlled chamber. The chamber is a 7 ft by 14 ft room with stainless steel walls equipped with a 3Hp Copeland compressor, 4 fan Larkin evaporator with hot gas defrost, as well as manually set hi and low temperature alarms. The chamber is able to reliably maintain temperatures of -4 °C to 20 °C, with brief periods of thawing approximately eight times per 24 hour period; therefore the -15 °C experiment was unable to be completed in the environmental chamber. An upright freezer with rough temperature control was secured to complete the -15 °C experiment (Figure 3). Due to complications with the chamber maintaining proper temperature after the -4 °C experiment was completed, two temperature loggers were placed in the chamber to record temperature. HOBO Water Temperature Pro V2 (Model # U22-001) sensor temperature loggers were set to record temperature once every 10 minutes to identify possible deviations from the programmed temperature. After deviations were identified, the sensor was set to record temperature once an hour. One temperature logger recorded chamber air temperature, while another temperature logger was placed in a 1 L amber sample jar filled with pure water. This logger recorded the impact of any deviations in temperature to the samples. These temperature loggers were utilized in the upright freezer for the -15 °C experiment as well but only to record air temperature. Lights in the climate-controlled chamber remained off for the full extent of the experiments, with the exception of brief periods when samples were inspected.



**Figure 3.** Freezer arrangement incorporating a shaker table to hold the SPME samples and a stir plate for the PE samples to complete the  $-15\text{ }^{\circ}\text{C}$  experiment.

For the first experiment at  $-4\text{ }^{\circ}\text{C}$  and 100 psu, six replicates were prepared. Two samples (passive sampler plus water) were removed after three weeks, four weeks and five weeks to ensure the samplers had reached equilibrium. The duration necessary for equilibrium to be reached was then employed for the remaining warmer temperatures. A similar time series was completed for the  $-15\text{ }^{\circ}\text{C}$  experiment, except that samples were removed and compared after four and five weeks. After the sampling time period was reached, PEs and SPMEs were removed from the 1 L sample jars, wiped dry with a Kimwipe<sup>®</sup> (to avoid contamination) and extracted in organic solvent. The sample water was then decanted to another pre-cleaned 1 L amber jar, so as not to include the compounds sorbed to the glass, and stored at the temperature the experiment was performed, if possible or at room temperature, until water samples were extracted. Water samples were all extracted through liquid-liquid extraction with dichloromethane (DCM), following methods outlined in the Environmental Protection Agency (EPA) method 610 (Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater – PAHs). Deviations from the method included manually shaking all samples with DCM for 5 min for each extraction, when the method listed shaking samples for 3 min for each extraction. Pure water utilized to prepare the salt water mixture under went further analysis to assess the concentration of dissolved organic carbon (DOC) present in the sample. Triplicate 5 mL samples of pure water were centrifuged at  $1000\times g$  for 30 min prior to analysis by Shimadzu TOC-V<sub>CPH/CPN</sub> Total Organic Carbon analyzer (Kyoto, Japan). Centrifuging samples served to separate out the particulate organic carbon, so that only the DOC was sampled. After the passive sampler and water concentrations were determined, the  $K_{PS-W}$  was calculated for each compound for each sampler. Experimentally derived  $K_{PS-W}$  were compared to theoretical  $K_{PS-W}$  that were found in the literature corrected for changes in temperature and salinity encountered in all experiments using the van't Hoff (equation 6) and Setschenow correction (equation 7), respectively (Schwarzenbach et al. 2003).

*Crude Oil Study.* A bulk oil sample was utilized to evaluate how the passive samplers perform under the conditions of an oil spill. The specific bulk oil sample was a Statfjord crude oil, the composition of which had been previously studied, and was being used in further experiments by collaborators (Faksness et al 2008; Aurand & Coelho 2005). The water soluble fraction (WSF) of the oil was prepared by the methods established by the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF) proceedings (Aurand & Coelho 2005; Faksness et al 2008). Specifically, 18 L of Narragansett Bay seawater (30 psu) was pre-filtered with a sand filter, then further filtered with two successive cartridge filters and finally suction filtered through a Whatman GF/C ( $1.2\text{ }\mu\text{m}$ ). Seawater was placed in a five gallon glass carboy, which was chemically rinsed prior to addition of the seawater. Sodium azide was added to the seawater to act as a biocide at a concentration of  $0.026\text{ mg mL}^{-1}$ . The WSF was prepared by adding 225 mL of Statfjord oil to the 18 L of Narragansett Bay seawater (1 to 80 oil to water ratio). The 1 to 80 ratio is less than the suggested 1 to 40 oil water ratio because of the limited amount of Statfjord oil available. Once the oil was added, the solution was capped with a foil covered rubber stopper and placed on a stir plate in the climate-controlled chamber which was set at  $5\text{ }^{\circ}\text{C}$ , and left to equilibrate for seven days. It was determined that a minimum of 96 hours was necessary to achieve equilibrium at the colder temperatures (Faksness et al 2008). After the seven days, the water was removed from the overlying oil above using a cleaned copper pipe (Faksness et al 2008). The water was suctioned into 15 1 L amber jars. Three of the samples were extracted by liquid-liquid extraction using DCM following EPA method 610 as previously stated to determine the concentration of the oil WSF. The remaining samples were split into six

replicates for each passive sampler. Blanks were prepared with Narragansett Bay seawater, filtered as previously stated and sodium azide added at the same concentration as previously mentioned. The passive samplers were then added to the water and exposed to the oil WSF at a temperature of 5 °C and allowed to reach equilibrium. As mentioned above, the flasks containing SPMEs were placed on a shaker table, while the flasks with PE were stirred on stir plates. After three weeks, three of the six replicates were removed from the chamber, the passive samplers removed and extracted, and water prepared for extraction. The remaining samples were allowed to continue equilibrating for another week before the passive samplers were removed and extracted, and water prepared for extraction. Once PAH concentrations in the samplers were determined, the experimentally derived  $K_{PS-W}$  were used to calculate the freely dissolved PAH concentration of the oil WSF and compared to the liquid-liquid extraction results.

*Field Deployment.* The field deployment was targeted to occur in winter, when water temperatures are usually the coldest in Narragansett Bay. For ease of access and ancillary data, SPMEs and PEs were deployed in Narragansett Bay at the Graduate School of Oceanography's dock, where a moored sensor records temperature and salinity data. The deployment of the passive samplers began once the R/V *Endeavor* departed in late March 2009. It was thought that the movement of the vessel had the potential to influence the results of this field trial.

Prior to deployment, passive samplers were impregnated with PRCs, as stated above. PEs, ca 1.5 g in weight, were deployed in triplicate for each time interval of the deployment. Due to the smaller sample volume, three 10 cm SPMEs were utilized for each sample, therefore nine SPMEs were collected for each sampling interval to achieve replicate samples. To prepare the passive samplers for deployment, PEs were individually placed on pre-cleaned stainless steel wires and attached to the deployment line (Figure 4). A copper housing was constructed to deploy the SPMEs (Figure 5). The delicate nature of the SPME fibers necessitated some sort of housing to be utilized for the deployment. The housing enabled the SPMEs to be attached to the deployment line in the same fashion as the PEs, facilitating the comparison of the samplers, as well as protected them from the environment. The concentration of PRCs remaining in the samplers after the deployment was confirmed to assess if adequate water circulation occurred during the deployment. Four housings were prepared with stainless steel racks similar to those prepared for the PRCs. SPMEs were divided between the four copper housings for deployment, and the copper housings attached to the deployment line with pre-cleaned stainless steel wire. The passive samplers were deployed on the interior of the dock near shore to be more protected from the elements. The deploy line was attached to a cinderblock, which served as an anchor, and a small buoy was fastened to the deploy line to keep the passive samplers off the sediment. A line was tied to the top of the buoy and attached to the dock to more easily recover the passive samplers. The passive samplers were deployed for 1, 2, 4, 7, 14 and 28 days to verify their performance under field conditions. A blank passive sampler was exposed to the air while the passive samplers were prepared for deployment and at every other sample recovery. At recovery, each sampler was placed into a pre-cleaned glass jar and remained in cold storage (-20 °C) until extracted.

Water was actively sampled for PAHs at two sample intervals, 7 and 14 days. This was achieved by pumping approximately 40 to 50 L of Narragansett Bay water first through glass fiber filter (Whatman GF/F) and then through polyurethane foam (PUF) plugs. PUFs were pre-cleaned prior to use twice with dichloromethane using Soxhlet extraction (Figure 6; Gioia et al. 2008).



**A**



**B**

**Figure 4.** PEs threaded on stainless steel wire (A) and attached to deployment line (B) for the field deployment in Narragansett Bay.



**A**



**B**

**Figure 5.** Copper housing manufactured to house SPMEs during the field deployment (A) and copper housing attached to deployment line with stainless steel wire for the field deployment in Narragansett Bay.

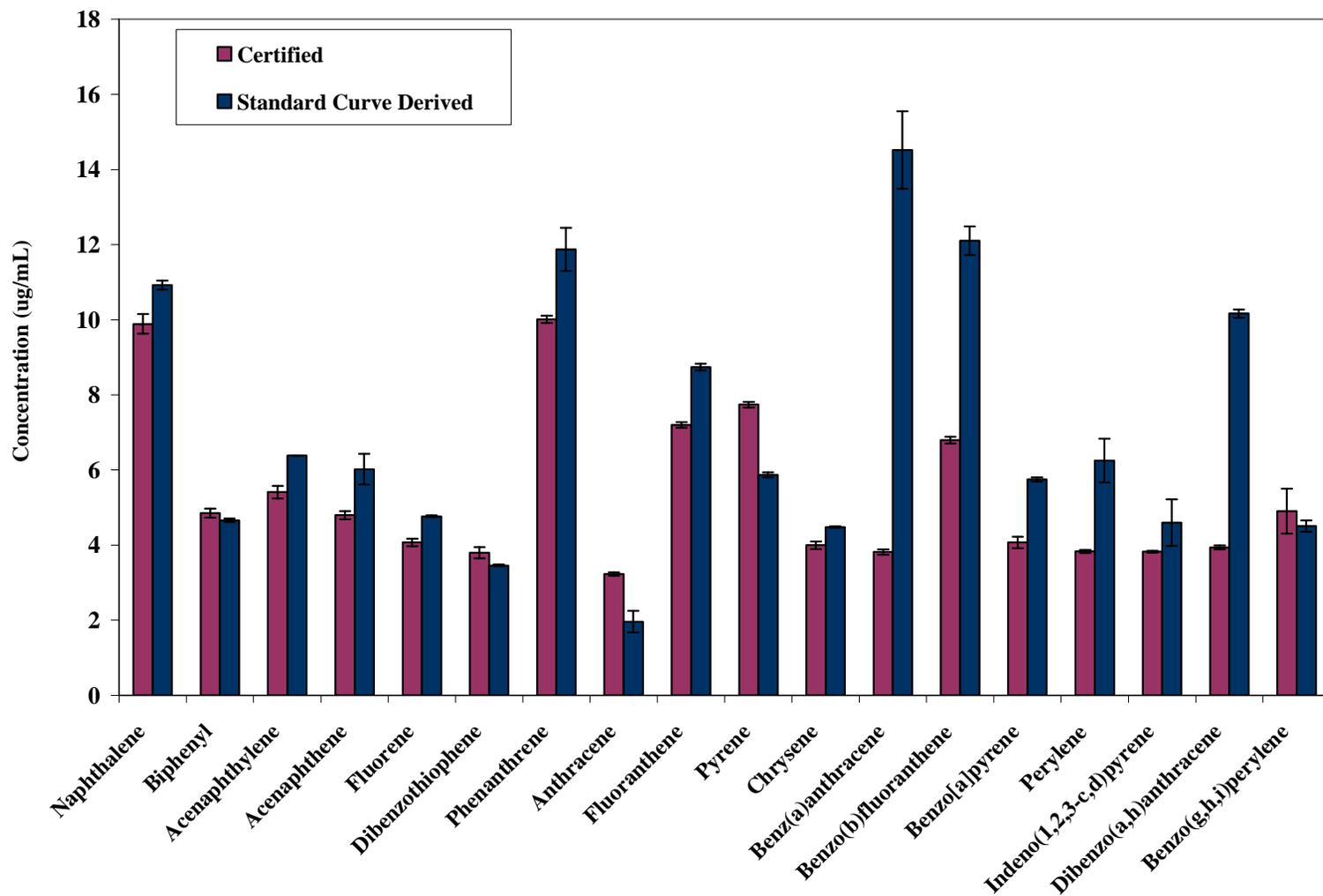


**Figure 6.** Active sampling arrangement with PUFs inserted in the tall cylinder (left) and filters placed in the flat platform (right) to collect dissolved PAH concentrations present in Narragansett Bay.

Two PUFs were employed for each water collection and were placed in cold storage ( $-20\text{ }^{\circ}\text{C}$ ) until samplers were extracted. PUFs were extracted by automated solvent extraction (ASE) (Dionex ASE 350). ASE cells were pre-cleaned with hexane, programmed for two 5 min static cycles maintained at  $150\text{ }^{\circ}\text{C}$  with a 25% rinse volume. Two PUFs that were pre-cleaned on the same day as the samples were used as sample blanks during the extractions. Prior to extraction, internal standard was added to all samples. PUFs were then extracted in two phases. The first phase was a single static cycle of a solvent mixture of 50% hexane and 50% acetone heated to  $100\text{ }^{\circ}\text{C}$  with a rinse volume of 25% to remove the water from the sample. The second phase consisted of two 10 min static cycles with hexane at  $100\text{ }^{\circ}\text{C}$  and a rinse volume of 60%. Sample extracts were dried with sodium sulfate and concentrated under nitrogen prior to analysis on the GC/MS. The loss rate for each PRC during each deployment was calculated and with the experimental  $\log K_{PS-W}$ , a loss rate for each compound derived for the time of deployment. Water concentrations derived from the passive samplers were then calculated using equation 2. PAH concentrations in the water samples were then compared to the PAH concentrations derived from the passive samplers.

#### 4.0 Results

*NIST Standard Calibration.* Eighteen of the PAHs in the NIST standard were present in the laboratory standard curve utilized for sample quantification (Tables 1 & 4). The calculated concentrations of the NIST standard using our laboratory standard curve were very similar to the certified concentration of the NIST standard (Figure 7). The majority of the compounds differed



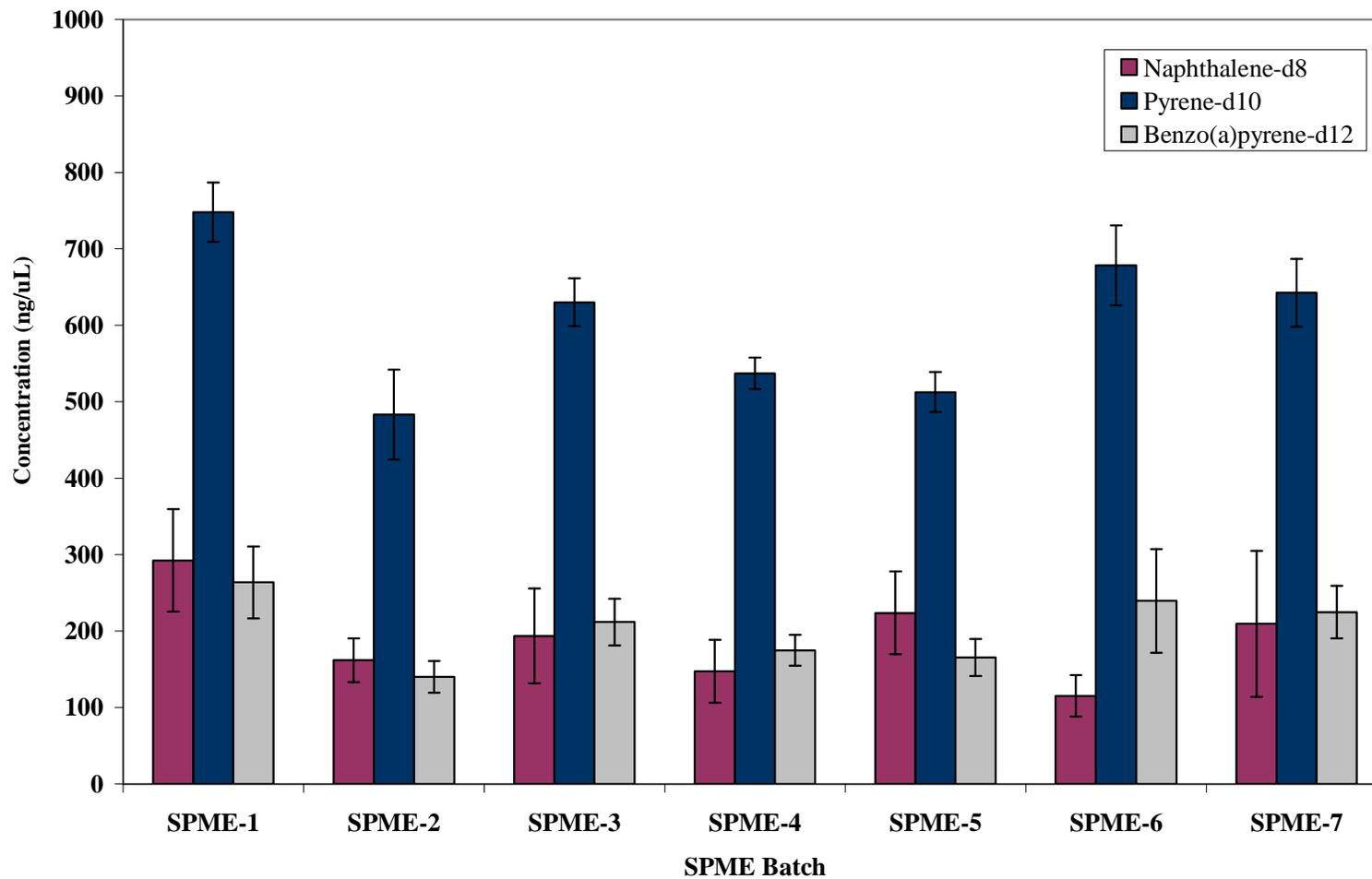
**Figure 7.** NIST standard concentration compared to the PAH laboratory curve derived concentration. Only PAHs present in the laboratory standard are displayed in the figure.

from the certified concentration by no more than 25%. For compounds where more than 25% difference was present, co-elution of similar compounds could explain the discrepancies. For example, the largest difference was found for benz[*a*]anthracene (Figure 7). Four others compounds of the same molecular weight as benz[*a*]anthracene are also included in the NIST standard. It seems likely that some of these compounds co-eluted with benz[*a*]anthracene adding to the apparent abundance of the compound. For the other two compounds where a large difference was present between the certified concentration and the laboratory standard curve derived concentration were benzo[*b*]fluoranthene and dibenzo[*a,h*]anthracene, and again co-elution is also a possible explanation for the difference (Figure 7). It is possible to separate these compounds out with a more specific GC/MS method, however the current method used for this study was not able to perform this function. The similar concentrations of the remaining compounds suggest the standard curve derived concentrations are reliable and could be employed for the experiments detailed below.

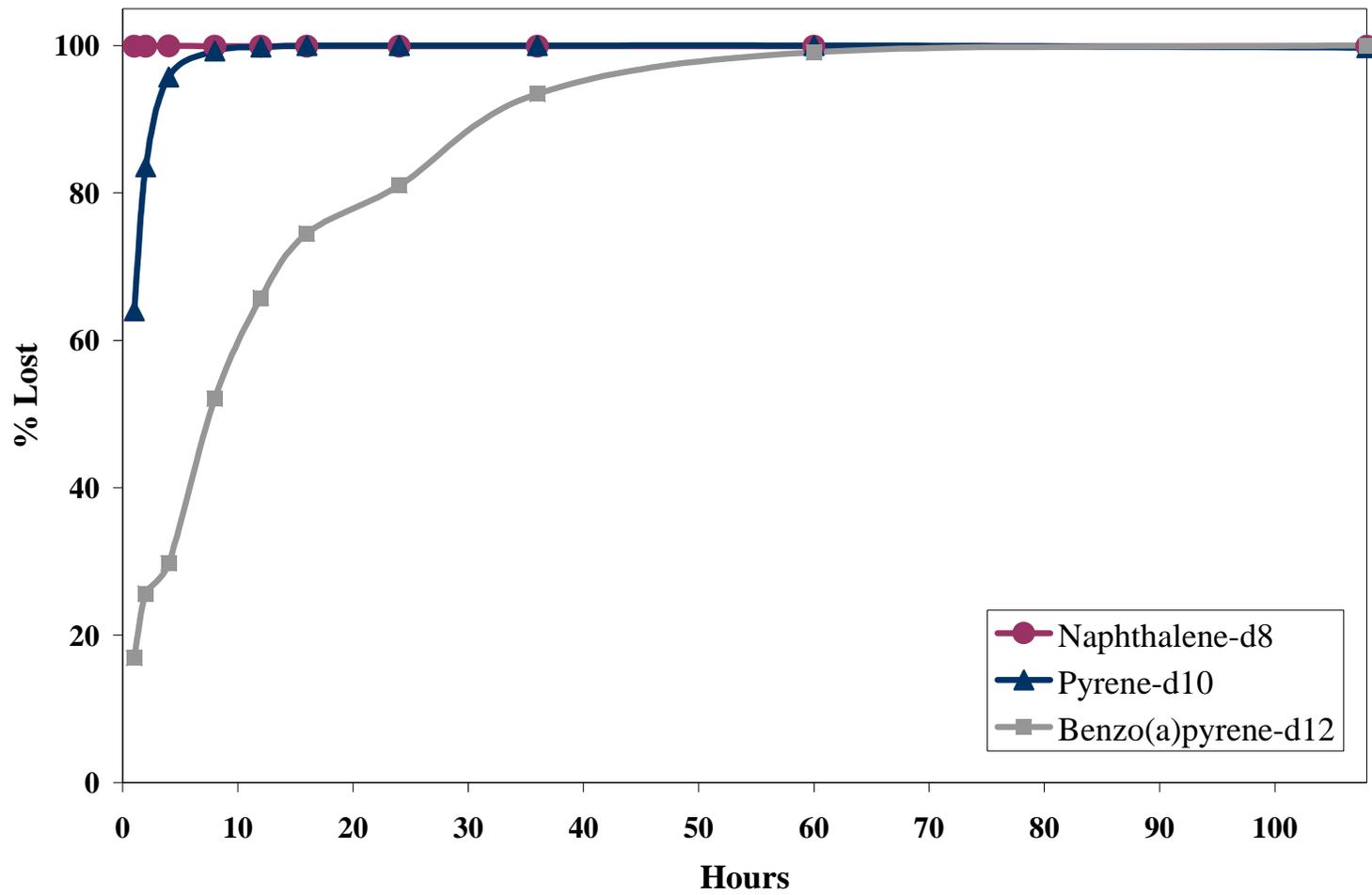
*Performance Reference Compounds.* Since PE samplers had been previously prepared with PRCs, PEs were successfully impregnated with PRCs, achieving a relative standard deviation between samples below 20%. SPMEs had not been worked with before and there were complications obtaining reproducible results for the PRCs in the SPMEs. Initial SPME results after equilibrating for one week displayed a 38% to 45% relative standard deviation for all PRCs. When the SPMEs were placed in the PRC solution, they tended to clump together. It was thought that this clumping caused a decreased surface area for the SPMEs to equilibrate with the solution. A stainless steel rack was fabricated with screen to hold the SPMEs and separate them from each other and increase the surface area exposed to the solution (Figure 1). For the next trial, seven separate batches of SPMEs were prepared. SPME were inserted into the metal rack and the batches were equilibrated on a shaker table for two weeks. SPME results for these batches produced relative standard deviations of less than 25% for all PRCs (Figure 8).

The next task accomplished was to investigate the loss rate of the PRCs. The percent loss was calculated to predict the times necessary for other PAHs to reach 95% equilibrium in the field under turbulent conditions (equation 4). This time period was found to range from less than an hour for naphthalene-*d*<sub>8</sub> to a few days (60 hours) for PAHs up to benzo(a)pyrene-*d*<sub>12</sub> (Figure 9), but longer times are needed for PAHs with molecular weights greater than 264.

*Effects of Temperature and Salinity on Equilibrium Partitioning Coefficients.* The equilibrium partitioning coefficient experiments were conducted at four temperatures and salinities. To calculate the  $K_{PS-W}$  for the compounds of interest,  $C_{PS}$  was divided by  $C_W$ . The  $C_W$  was determined through liquid-liquid extraction of the water sample. As stated previously, three sampling periods were completed during the first experiment (-4 °C) to investigate whether the samplers reached equilibrium. For the three different sampling time periods, log  $K_{PS-W}$  did not seem to differ consistently from sampling week to sampling week for the SPMEs or the PEs. Other researches have shown  $K_{PS-W}$  values show a linear correlation with the octanol-water partition coefficients ( $K_{OW}$ ) of the various PAHs, so experiment log  $K_{PS-W}$  values were plotted against the log  $K_{OW}$  to represent the data (Adams et al. 2007). Trendlines were plotted for each of the replicates to determine if there was a major difference in the slope of the line. The overlap of the trend line in both figures suggests there was no change in the  $K_{PS-W}$  values with time and the samples reached equilibrium after three weeks. This time period was similar to other



**Figure 8.** Average PRCs concentrations of seven separate SPME batches of with relative standard deviations less than 25%.



**Figure 9.** Percent lost of PRCs by SPMEs during laboratory loss rate experiment mimicking turbulent conditions in the field.

experiments performed by other researchers (Adams et al. 2007). The three week sampling period was used for the experiments at warmer temperatures.

The full range of compounds of interest, from phenols to benzo(g,h,i)perylene, were initially included in all plots (Table 1). It was not appropriate to graph the  $\log K_{PS-W}$  of the phenols versus  $\log K_{OW}$ , therefore a linear relationship was not achieved. The passive samplers are composed of apolar molecules, but octanol contains a hydroxyl group which results in additional physiochemical interactions occurring between phenols and octanol, like hydrogen bonding. A more appropriate fit for the phenolic compounds would be to plot the  $K_{PS-W}$  values verse a neutral solvent-water partition coefficient. A system such as hexadecane-water may result in a linear relationship with the phenol  $K_{PS-W}$  values (Schwarzenbach et al. 2003). Due to their assumed additional physiochemical interactions with octanol and their unfavorable partitioning in further experiments, the phenolic compounds were excluded from the remaining discussion. If replicates in each experiment were similar, the replicate samples were averaged. The experimental  $K_{PS-W}$  values were then compared to the theoretical  $K_{PS-W}$  values, which were calculated for the both the PEs and SPMEs. Cornelissen et al. (2008) published  $K_{PS-W}$  for a suite of PAHs for both PEs and SPMEs at 20 °C in the same experiment. The Cornelissen et al. values along with the linear relationship with  $\log K_{OW}$  were used to extrapolate the remaining  $K_{PS-W}$  for PAHs not listed in their study, but included in the present study with the following expressions:

$$\log K_{PE-W} = 1.10 \times \log K_{OW} - 0.69 \quad (8)$$

$$\log K_{SPME-W} = 0.756 \times \log K_{OW} + 0.66 \quad (9)$$

Both the SPMEs and PEs used in the Cornelissen et al. (2008) study were thicker (200  $\mu\text{m}$  for SPMEs and 100  $\mu\text{m}$  for PEs) than ones utilized in this study. To verify that these values were applicable to the passives in the present study, the  $K_{PS-W}$  of Cornelissen et al. (2008) were compared to other studies with passive samplers of similar thickness to the current study (Adams et al. 2007; Maruya et al. 2009). Once  $K_{PS-W}$  values for this study was determined for the full suite of PAHs in this study, the  $K_{PS-W}$  values were adjusted with the van't Hoff (equation 6) and Setschenow equations (equation 7) to reflect the temperature and salinity that the  $K_{PS-W}$  values were experimentally determined (Schwarzenbach et al. 2003). Since not all enthalpies of phase change ( $\Delta H$ ; kJ/mol) were available for the PAHs included in this study, they had to be extrapolated from calculated LeBas molar volume (Schwarzenbach et al. 2003). The Setschenow constants were determined through extrapolation with the  $\log K_{OW}$  of the compound (Ni & Yalkowsky 2003):

$$K_S = 0.040 \times \log K_{OW} + 0.114 \quad (10)$$

The theoretical  $\log K_{PS-W}$  values were calculated in this manner using equations 6 and 7 for all of the temperatures and salinities studied.

To further validate results, the dissolved organic carbon (DOC) concentration of the water samples was analyzed. Compounds with  $\log K_{OW}$  values above 5 are more hydrophobic and

therefore have a higher affinity to adsorb to glassware and the dissolved and/or colloid (DOC) present in the sample, which can alter the results of the  $K_{PS-W}$  calculation. All samples returned DOC concentrations below the detection limit of the calibration curve, which was 0.5 ppm. This suggests that there was not sufficient DOC present in the water samples to alter the calculation of the  $K_{PS-W}$ .

Through discussions at the EU-SETAC meeting in May with experts who were examining temperature dependence of partitioning (Jonker, personal communication), it was suggested that a decrease in the solubility of the compounds at the low temperatures and high salinities could cause complications in assessing equilibrium concentrations of the compounds with higher  $\log K_{OW}$  values (Muijs & Jonker 2009). To investigate this, the SPME and PE water samples were extracted by liquid-liquid extraction making sure not to include any solids or compounds that could be associated with the sample container. Water samples from two replicates from both the SPMEs and PEs were extracted and the extracted water concentrations utilized to derive the  $\log K_{PS-W}$  values. Since the temperature and salinity range was so large another check was included to the  $K_{PS-W}$  calculations to ensure that the solubility of the compounds had not been exceeded. The solubility ( $S$ ;  $\text{mol}\cdot\text{L}^{-1}$ ) was adjusted for temperature effects by:

$$\log S_L = A_{SL} - B_{SL}/T \quad (11)$$

where  $A_{SL}$  represents the intercept of the temperature dependence and  $B_{SL}$  is the slope of the temperature dependence (Paasivirta et al. 1999).  $A_{SL}$  and  $B_{SL}$  are calculated by:

$$A_{SL} = \Delta H_F / [(2.3026 \cdot R \cdot T_m) + 5.154 - 0.036 \cdot V_b - 0.217 \cdot \ln V_b + C] \quad (12)$$

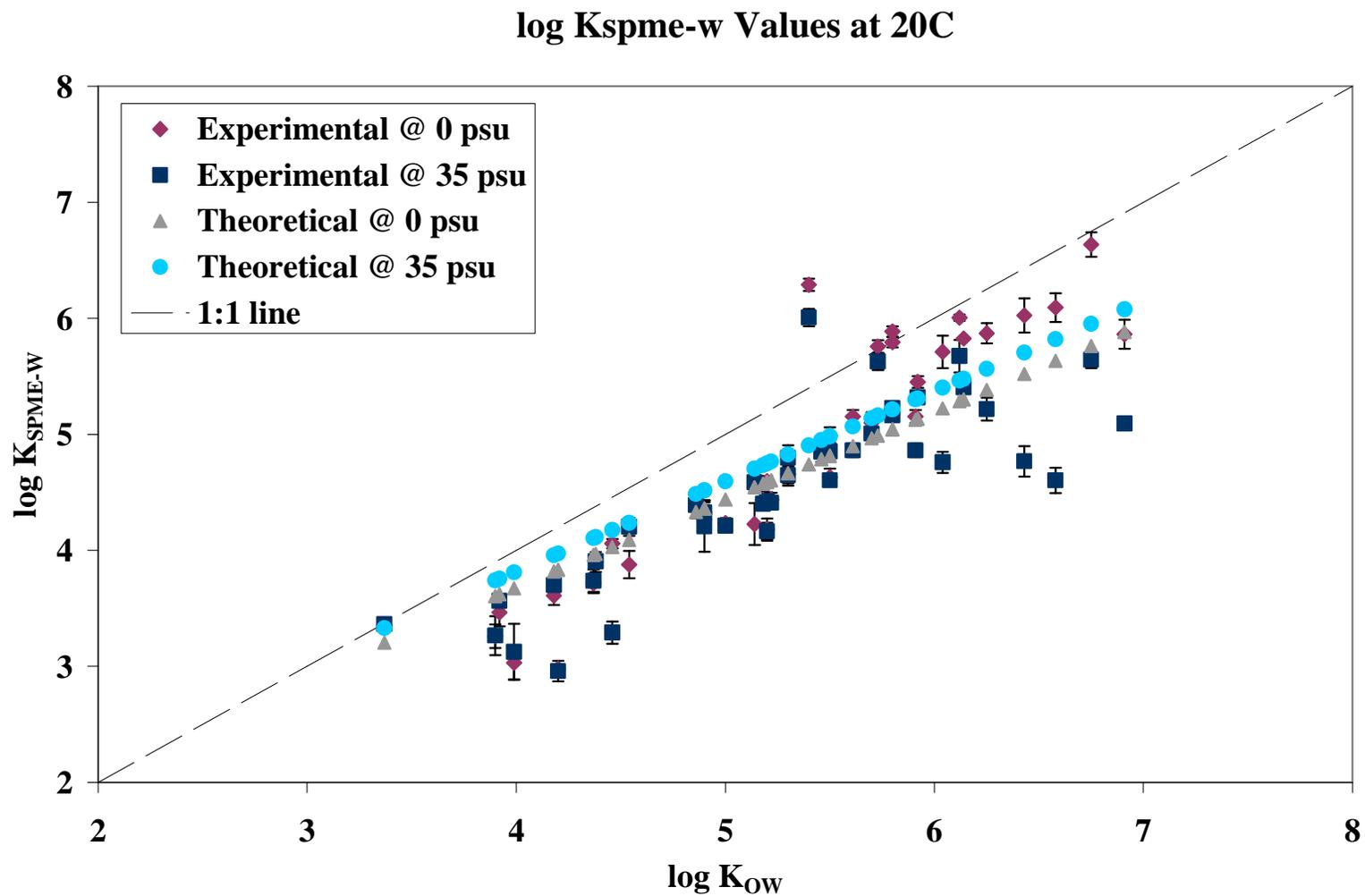
$$B_{SL} = \Delta H_F / (2.3026 \cdot R) \quad (13)$$

where  $\Delta H_F$  is the heat of fusion ( $\text{J}\cdot\text{mol}^{-1}$ ),  $R$  is the gas constant ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ),  $T_m$  is the melting point (K),  $V_b$  is the LeBas molar volume ( $\text{cm}^3\cdot\text{mol}^{-1}$ ), and  $C$  is a derived constant for each compound class (Paasivirta et al. 1999). Paasivirta et al. (1999) list  $C$  to be 0.734 for PAHs. Since not all variables are known for the suite of PAHs investigated, some variables had to be extrapolated from existing data (Mackay et al. 1992; Ruelle & Kesselring 1997). The melting point was extrapolated from known melting points and molecular weights and  $\Delta H_F$  was extrapolated from the known  $\Delta H_F$  values and melting points. Solubility concentrations at standard temperatures were calculated and compared with predicted and experimental values (Ruelle & Kesselring 1997). The solubility was then adjusted for salinity effects using a modified Setschenow equation (equation 7; Schwarzenbach et al. 2003). The Setschenow constants were determined through extrapolation with the  $\log K_{OW}$  (equation 7) of the compound (Ni & Yalkowsky 2003). These calculated solubility values merely served as a thermodynamic check that calculated or extracted water concentrations did not exceed the solubility values and did not interfere with the calculation of the experimental  $K_{PS-W}$  values.

An experiment was conducted at 20 °C to validate methods utilized in the experiments by comparison to values derived by other researchers. Samples were prepared at both 0 and 35 psu. The theoretical and experimental  $\log K_{PS-W}$  values for the 20 °C experiment were calculated as previously mentioned. No water concentrations exceeded the solubility. In the 20 °C experiment, the 0 psu SPME samples SPME-0psu-20C-A and in the 35 psu SPME samples SPME-35psu-

20C-4 were statistically different from the other three samplers of the same salinity, so they were excluded from the average of the results. In the PE results, all replicates displayed similar trend lines, so no samples were excluded. When the averaged SPME results are examined, the majority of the compounds fall below the plotted theoretical values, with some scatter in the compounds with higher log  $K_{OW}$  values (Figure 10). 2, 6-Diisopropyl naphthalene is the one compound whose experimental log  $K_{PS-W}$  for both salinities plots much higher than the expected theoretical log  $K_{PS-W}$  and does not follow the trend of the other experimental values. Since this variation only occurs in this one experiment, there was a low standard deviation and there was none detected in either of the blanks at 0 or 35 psu, it is doubtful that this is from contamination. More investigation is needed to explain the behavior of this isolated compound. The remainder of the SPME results, for the most part, appears to follow the same trend, with the log  $K_{PS-W}$  increasing with increasing log  $K_{OW}$ , in agreement with the findings of other researchers (Figure 10; Cornelissen et al. 2008; Adams et al. 2007; Schwarzenbach et al. 2003). This trend is more obvious when the graph is focused on the priority PAHs as well the lower molecular weight (LMW) compounds present in Statfjord crude oil (Table 6; Figure 11). The compounds with higher log  $K_{OW}$  display the most scatter, with 0 psu samples plotting above the theoretical line and 35 psu samples plotting below the theoretical. In the PE results, the majority of the experimental log  $K_{PS-W}$  values follow the same trend as the theoretical log  $K_{PS-W}$  values, though most of the compounds lie above both theoretical lines (Figure 12). As in the SPME results, when the graph is narrowed down to the priority PAHs and the LMW compounds, the trends are clearer (Figure 13). The compounds plot above the theoretical value lines. With the minimization of the displayed data, there is a visible difference in the various salinities values. The 35 psu samples tend to lie slightly above the 0 psu samples, as is theorized. In general, the 20 °C experimental results were in agreement with the theoretical values. This indicates potential deviations from theoretical values in the other experiments are not due to differences between the calculated or theoretical log  $K_{PS-W}$  values or the methods used. Since the theoretical values were taken from peer-reviewed studies, the agreement between experimental and theoretical values validates the passive samplers and extraction methods used in this study.

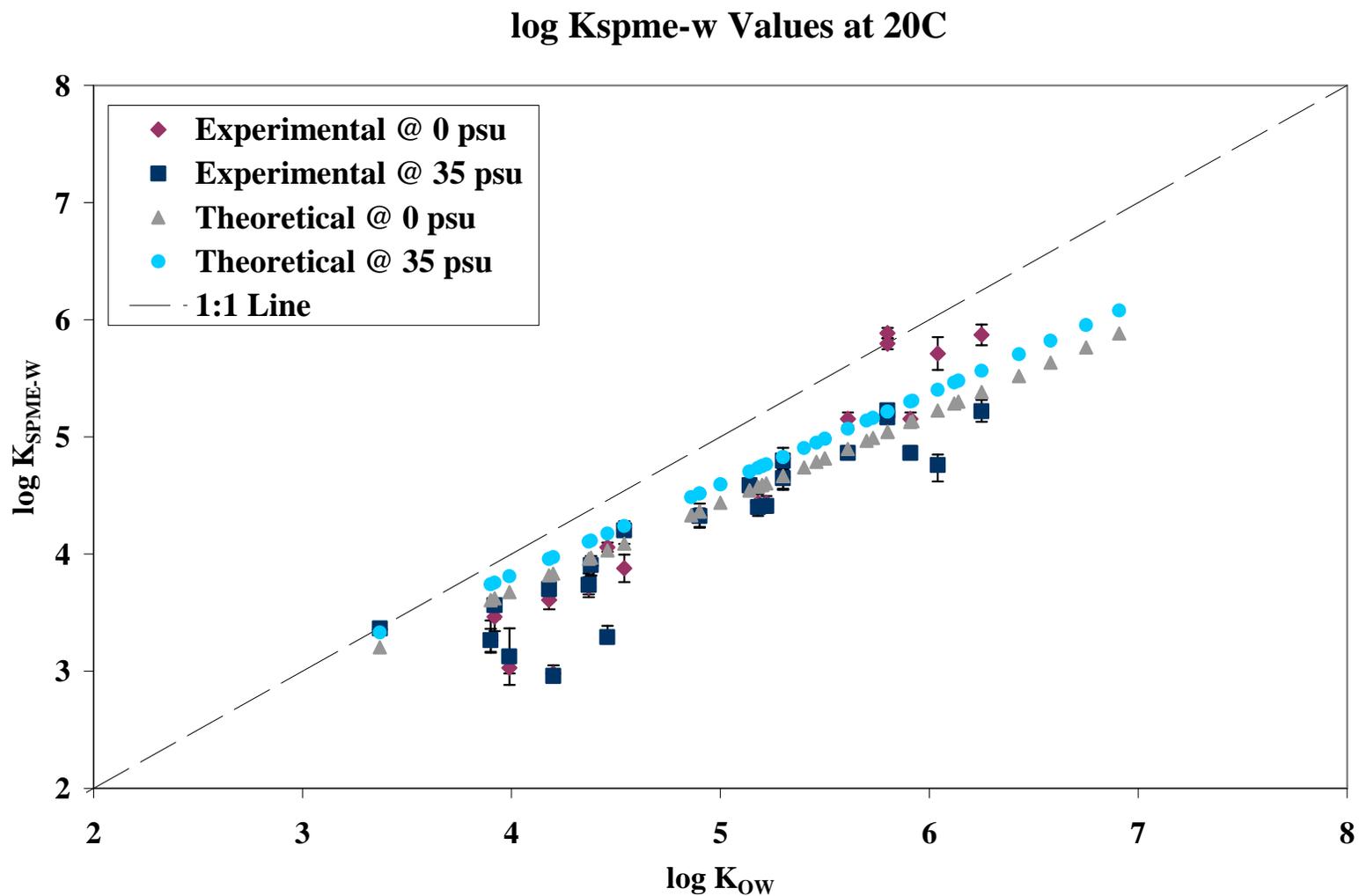
The next coldest partitioning experiment was conducted at 2 °C at salinities of 0 and 100 psu. The theoretical and experimental log  $K_{PS-W}$  values for the 2 °C experiment were calculated as previously mentioned. The water concentrations were checked against the compounds solubility at 2 °C at salinities of 0 and 100 psu. No water concentrations exceeded the solubility. For the four SPME replicates at 0 and 100 psu, the log  $K_{PS-W}$  was only slightly different for replicate D in the 0 psu samples. The remaining SPME samples at 0 psu and all the 100 psu replicates displayed agreement between replicates. In the PE samples at 2 °C, agreement between all replicates at both 0 and 100 psu is visible in the similar slope of the trend lines. The replicates for both the SPMEs and PEs at 0 and 100 psu were then averaged. In initial analysis, some compounds approached the expected linear line, the compounds with lower log  $K_{OW}$  values seem to follow the trend of theoretical results, with the majority of the 100 psu log  $K_{PS-W}$  values being above the 0 psu log  $K_{PS-W}$  values (Figures 14 & 15). This is the expected trend, where the addition of the salt increases the partitioning into the sampler. However, there seems to be a point where the log  $K_{PS-W}$  values depart from following the trend of the theoretical values. The log  $K_{PS-W}$  values appear to flatten out around log  $K_{OW}$  of around 5.5 to 6. In the SPME results, there is a more distinct point where this occurs (log  $K_{OW}$  of 5.5), whereas in the PE results, there is a greater spread in the experimental values and the log  $K_{OW}$  value is closer to 6 (Figures 14 & 15). In both the SPME and PE results, there seems to be no difference in this point between 0



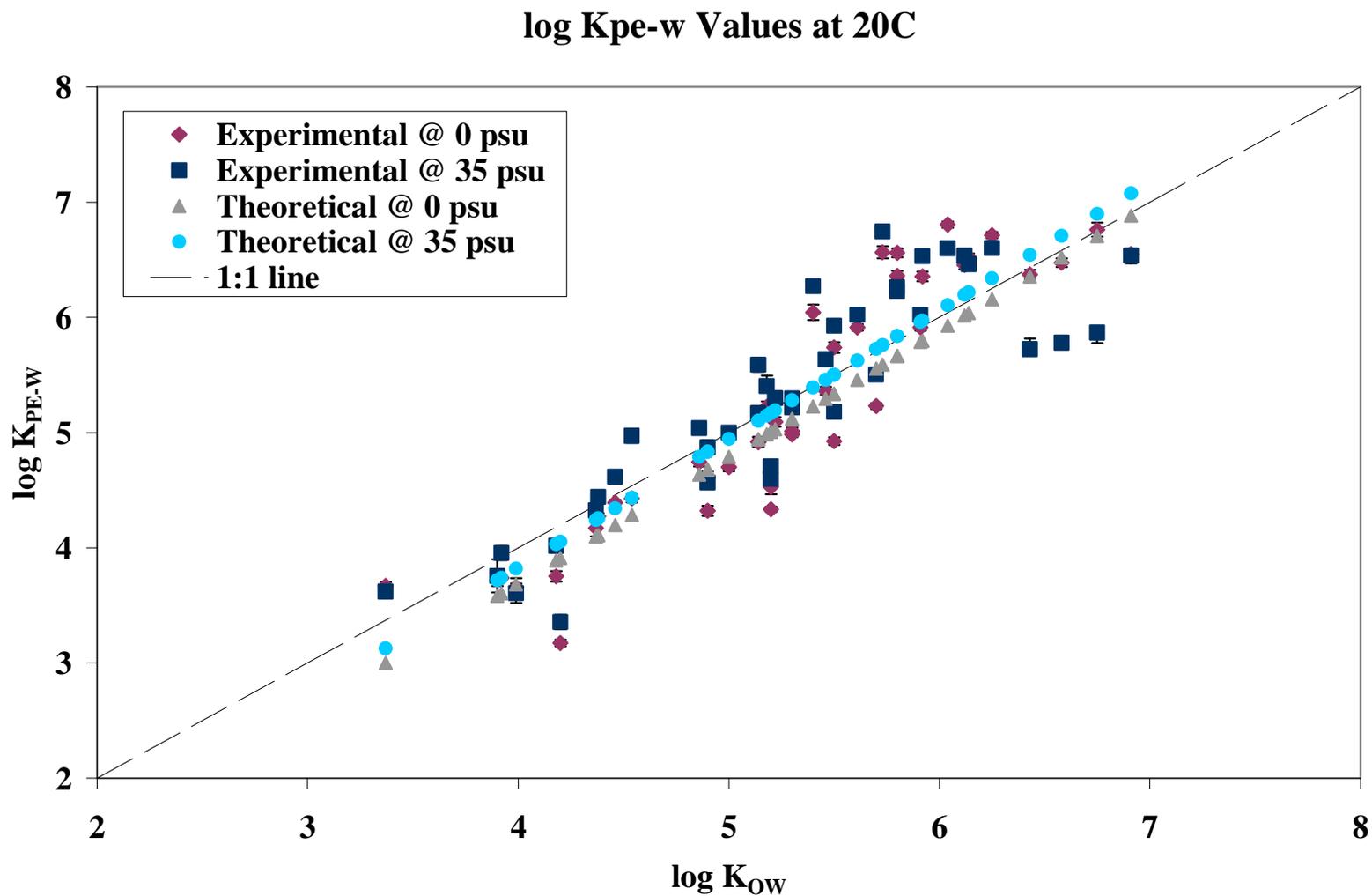
**Figure 10.** Averaged experimentally derived  $K_{SPME-W}$  at 20 °C and salinities of 0 and 35 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.

**Table 6.** List of the priority PAHs and LMW compounds present in the Statfjord crude oil with their respective log  $K_{OW}$  values and molecular weight

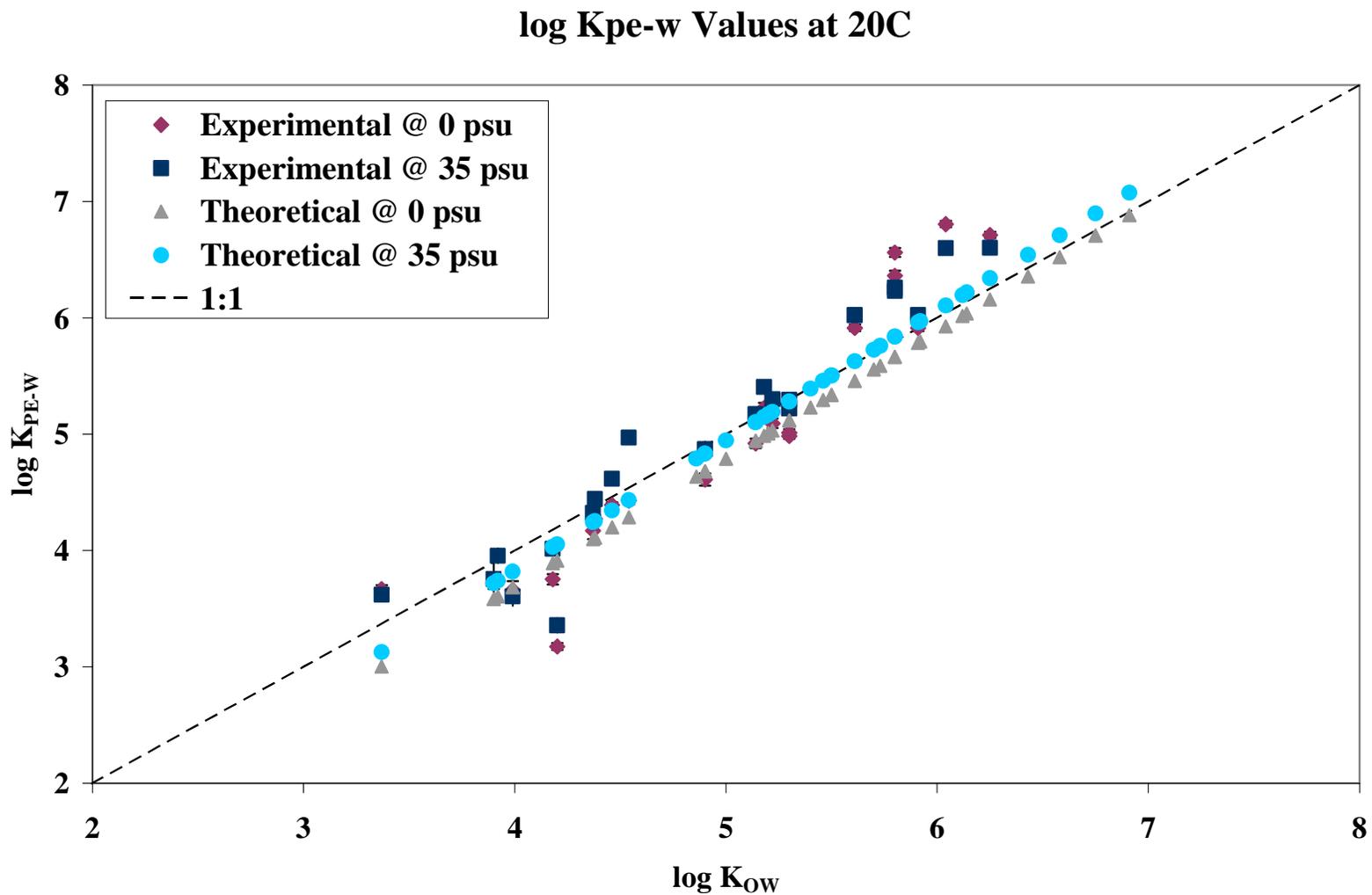
<b>Compounds</b>	<b>log <math>K_{OW}</math></b>	<b>Molecular Weight</b>
Naphthalene	3.37	128
2-Methyl naphthalene	3.99	142
Biphenyl	3.9	154
1,5-Dimethyl naphthalene	4.37	156
Acenaphthylene	4.2	152
Acenaphthene	3.92	154
2,3,5-Trimethyl naphthalene	4.9	170
Fluorene	4.18	166
1,4,6,7-Tetramethyl naphthalene	5.3	184
1,2,5,6-Tetramethyl naphthalene	5.3	184
Dibenzothiophene	4.38	184
Phenanthrene	4.46	178
Anthracene	4.54	178
1-Methyl phenanthrene	5.14	192
Fluoranthene	5.22	202
Pyrene	5.18	202
Chrysene	5.61	228
Benz(a)anthracene	5.91	228
Benzo(b)fluoranthene	5.8	252
Benzo(h)fluoranthene	5.8	252
Benzo[a]pyrene	6.04	252
Perylene	6.25	252



**Figure 11.** Averaged experimental  $K_{SPME-W}$  at 20 °C and salinities of 0 and 35 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.

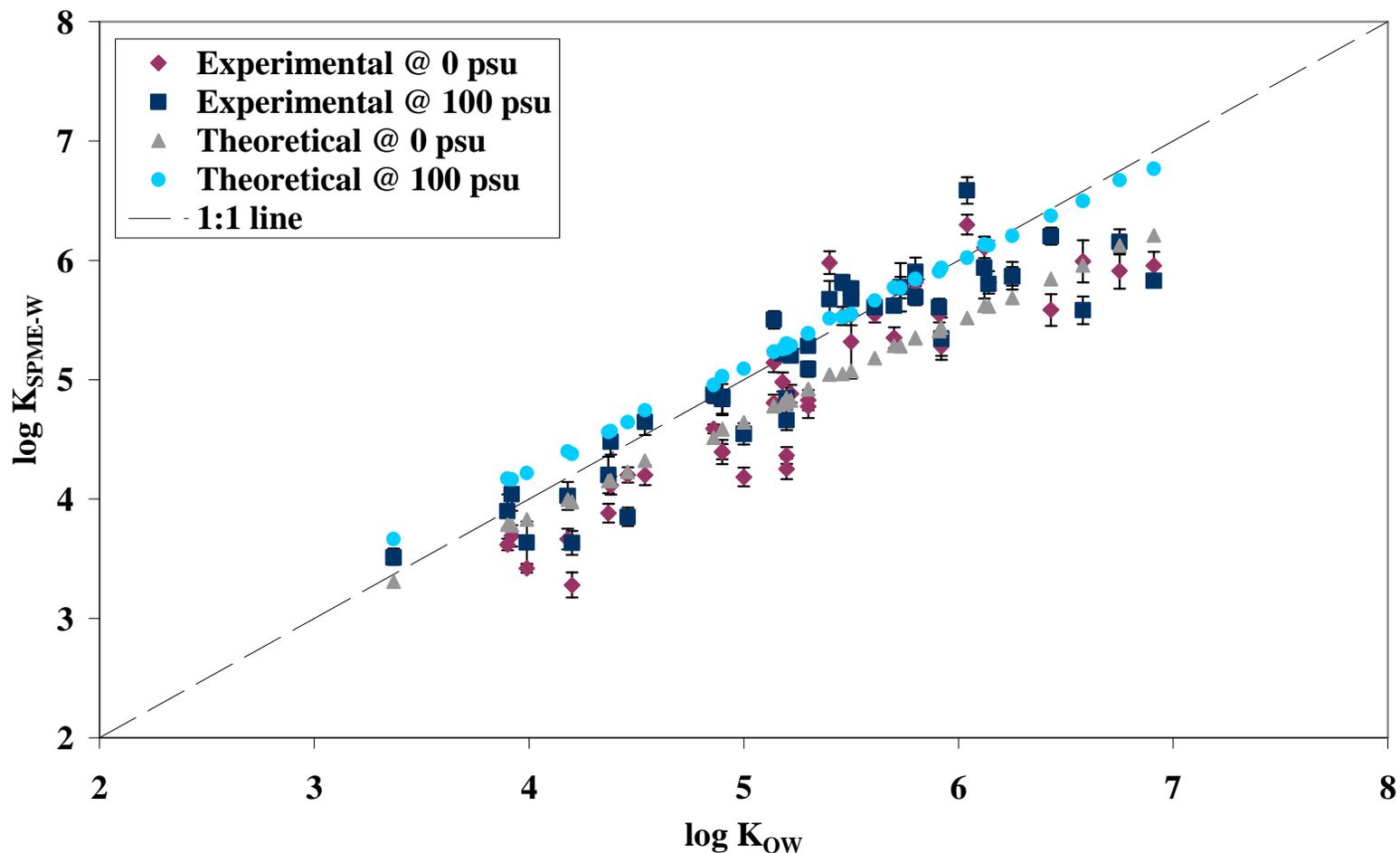


**Figure 12.** Averaged experimentally derived  $K_{PE-W}$  at 20 °C and salinities of 0 and 35 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.

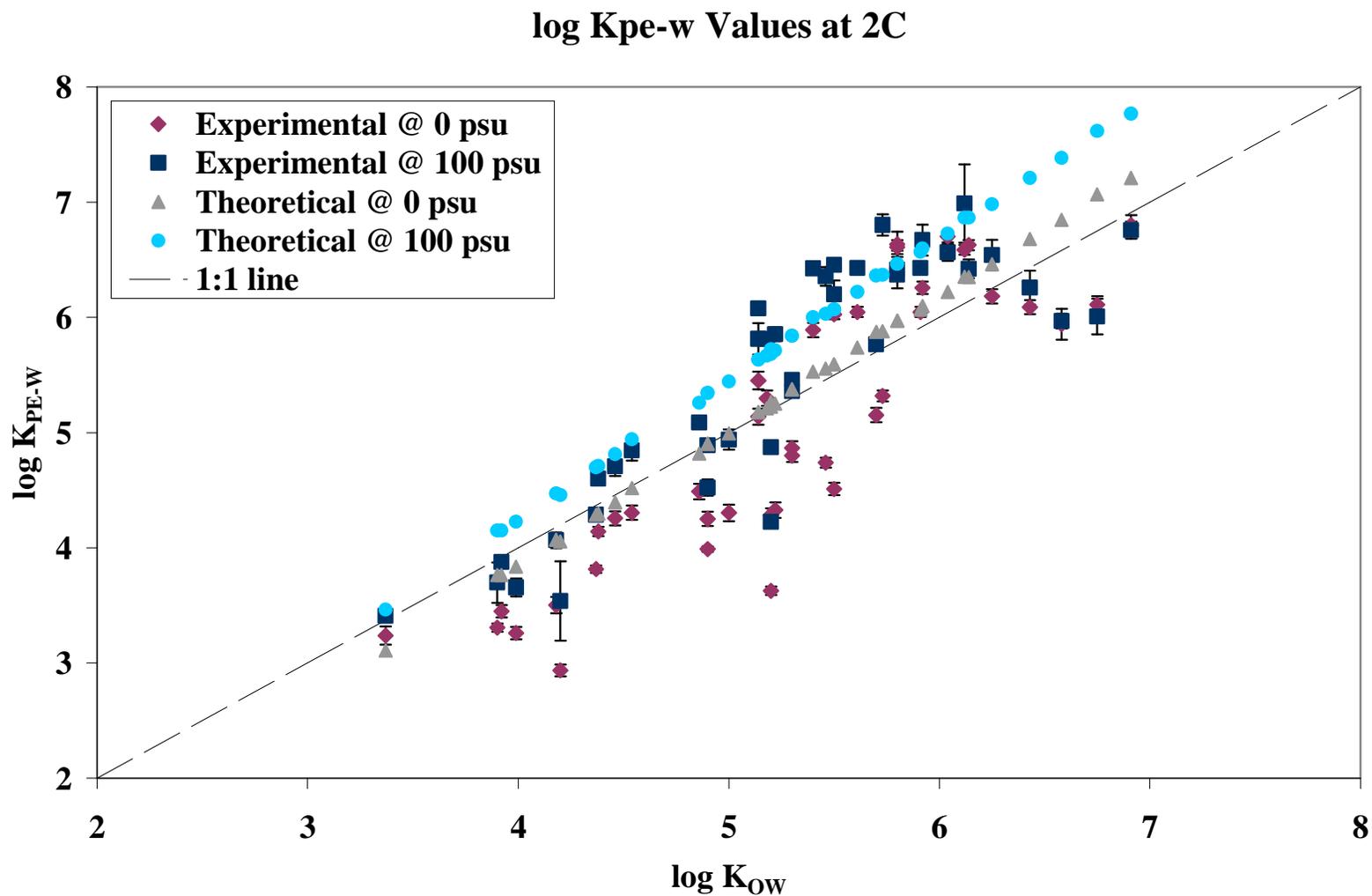


**Figure 13.** Averaged experimental  $K_{PE-W}$  at 20 °C and salinities of 0 and 35 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.

### log K<sub>spme-w</sub> Values at 2C



**Figure 14.** Averaged experimentally derived  $K_{\text{SPME-W}}$  at 2 °C and salinities of 0 and 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.

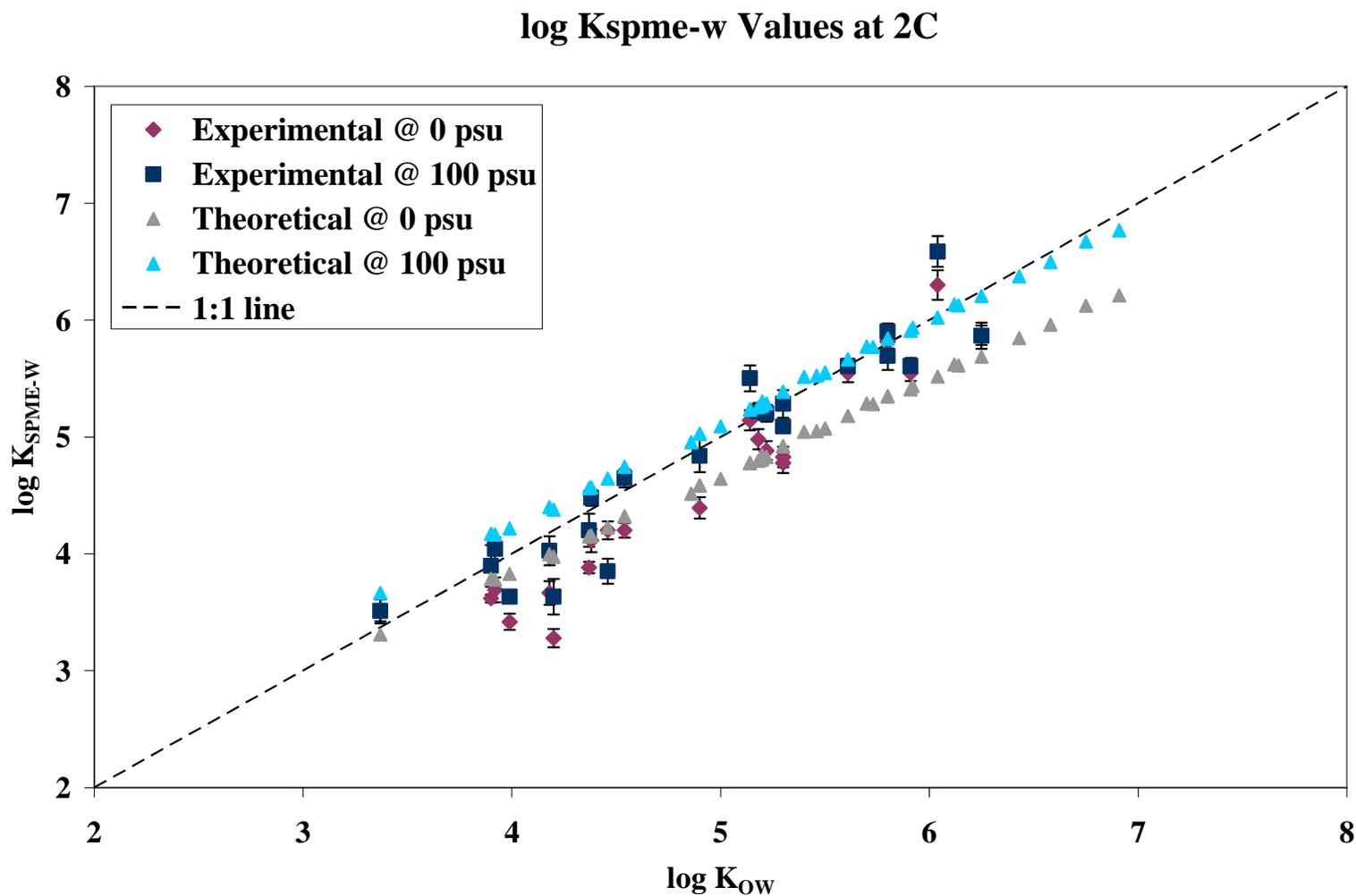


**Figure 15.** Averaged experimentally derived  $K_{pe-w}$  at 2 °C and salinities of 0 and 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.

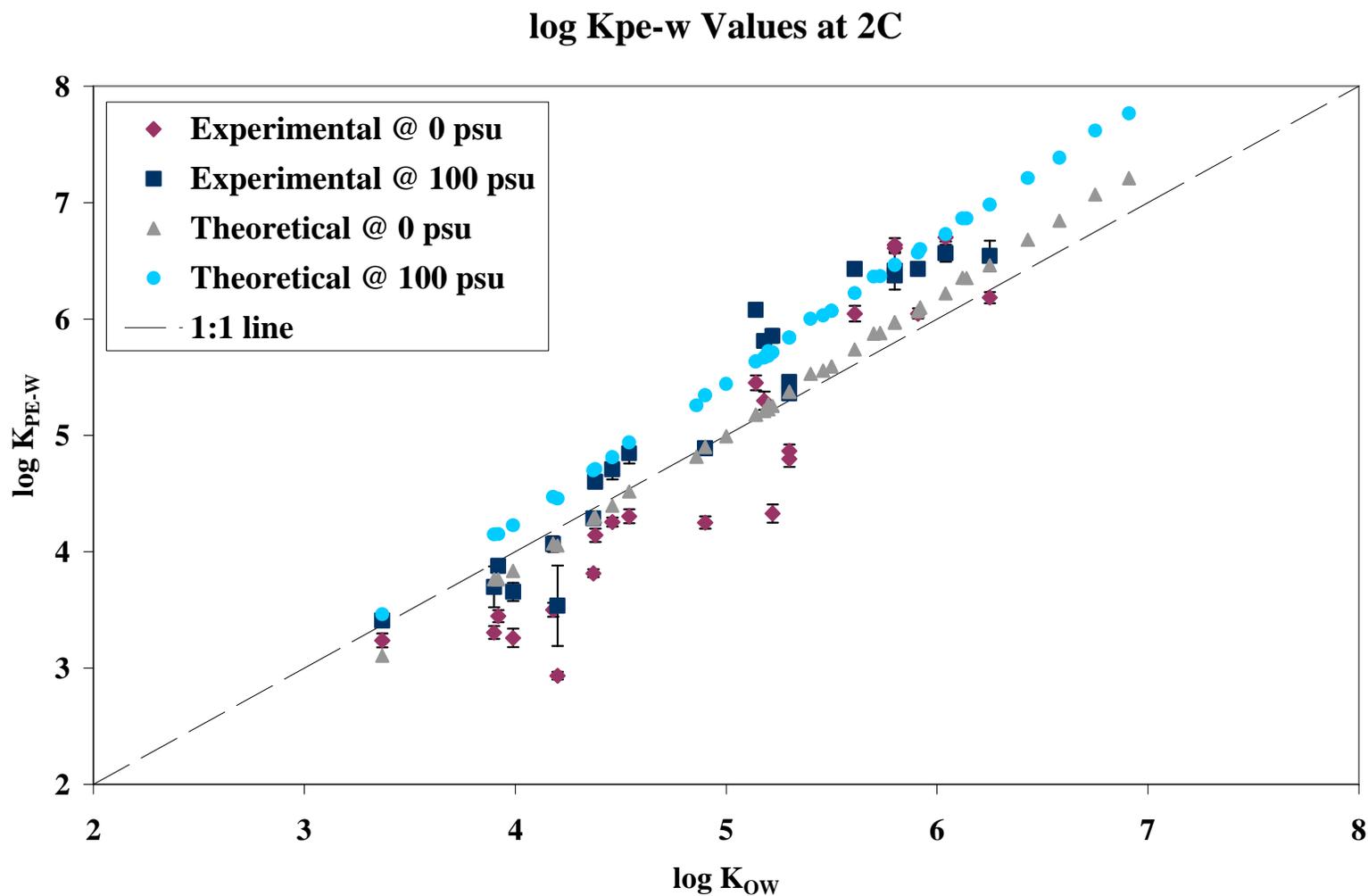
and 100 psu. Since neither a lack of equilibrium, DOC, or solubility can explain these results, it was theorized that the higher log  $K_{OW}$  compounds did not reach equilibrium. To verify this suspicion, the log  $K_{PS-W}$  values of the PRCs were calculated for both the 20 and 2 °C experiments and graphed against the molecular weight of the compound. In the 20 °C experiment, the PRCs and the corresponding undeuterated compounds log  $K_{PS-W}$  values were only a few tenths of a log unit different. When the log  $K_{PS-W}$  values of the PRCs were examined for the 2 °C experiment, the log  $K_{PS-W}$  values of naphthalene and pyrene were similar for both the natives and PRCs. However, for benzo(a)pyrene (Bap), the log  $K_{PS-W}$  values were not as similar as displayed in the 20 °C experiment. This served as evidence that the higher molecular weight (HMW) compounds had not reached equilibrium. To adjust the HMW compounds, the average of the log  $K_{PS-W}$  values between the d-BaP and the native was subtracted from the corresponding native log  $K_{PS-W}$  value to create a correction factor. The theory behind the calculation is the remainder of loss of the PRCs is equal to the remainder of uptake of the natives to equilibrium, so the average of the two would give an approximate equilibrium log  $K_{PS-W}$  value. Since PRCs are not utilized for each native, an extrapolation is necessary to apply to the other HMW compounds. An extrapolation was developed which included the correction factor and the difference in molecular weight was used to adjust the HMW compounds to reflect equilibrium.

After this correction is incorporated into the data, the linear trend to the data is restored. Again, focusing on the priority PAHs and the LMW compounds present in the Statfjord oil, the trends in the data are more apparent. In the SPME data, the effect of salt between the replicates is visible. The majority of the 0 psu data plots slightly below the theoretical 0 psu line (Figure 16). The majority of the 100 psu samples lie above their corresponding 0 psu log  $K_{SPME-W}$  value. There appears to be a greater salinity effect in the PE data, with the 100 psu log  $K_{PE-W}$  values plotting above the 0 psu values (Figure 17). In general, the correction factor applied to the 2 °C experiment restored the linear relationship expected, with great difference between the 0 and 100 psu samples visible the increase in the log  $K_{PS-W}$  value increase. This demonstrated the salinity should be incorporated into the calculation of the equilibrium partition coefficient with the Setschenow equation.

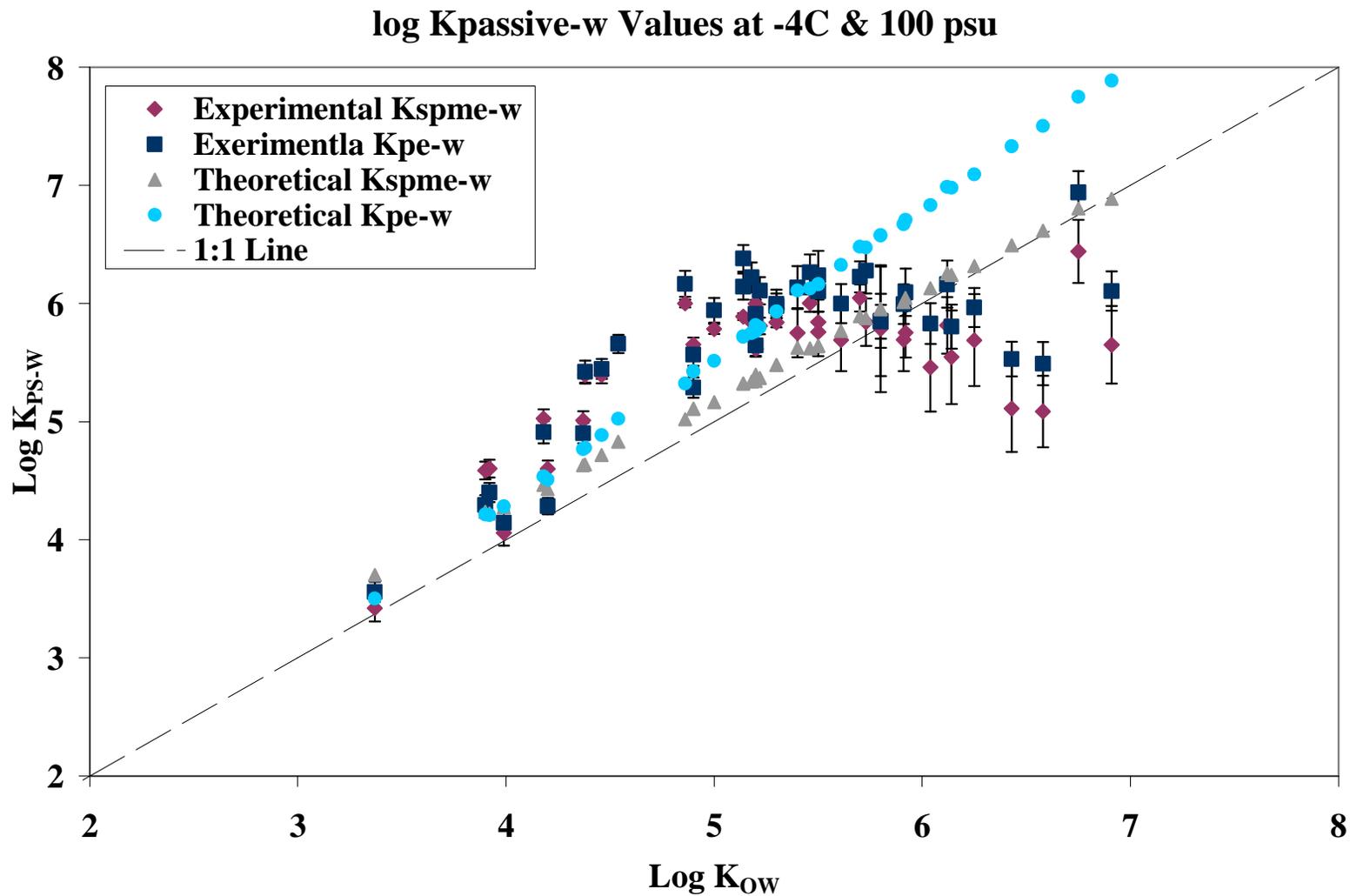
The next coldest experiment was completed at -4 °C with a salinity of 100 psu. The theoretical and experimental log  $K_{PS-W}$  values for the -4 °C experiment were calculated as previously mentioned. The water concentrations were checked against the compounds solubility at -4 °C at a salinity of 100 psu. No water concentrations exceed the solubility. In the -4 °C experiment, SPME-1-C-3wk and SPME-5-D-5wk samples seemed to be outliers for the majority of the compounds of interest. Since the other samples of this time period agreed with the remaining samples, it is believed that is due to sampling error, possibly loss of the compounds during the experiments. As seen in the previous 2 °C data set, the HMW compounds or compounds with higher log  $K_{OW}$  values deviated from the expected linear line (Figure 18). The compounds with higher log  $K_{OW}$  values tend to level off or decrease with increasing log  $K_{OW}$  over a log  $K_{OW}$  value of 5. As mentioned previously, it is theorized this is due to equilibrium not being reached. When the PRC log  $K_{PS-W}$  values were examined, only naphthalene appeared to have reached equilibrium so corrections were made for all compounds. Limiting the data set to the priority PAHs and the LMW compounds present in Statfjord oil, the trend corrections for equilibrium are evident (Figure 19). In both the SPME and PE data set, the compounds with log  $K_{OW}$  values below 5.5 lie above both the log  $K_{SPME-W}$  and log  $K_{PE-W}$  theoretical lines, while the compounds



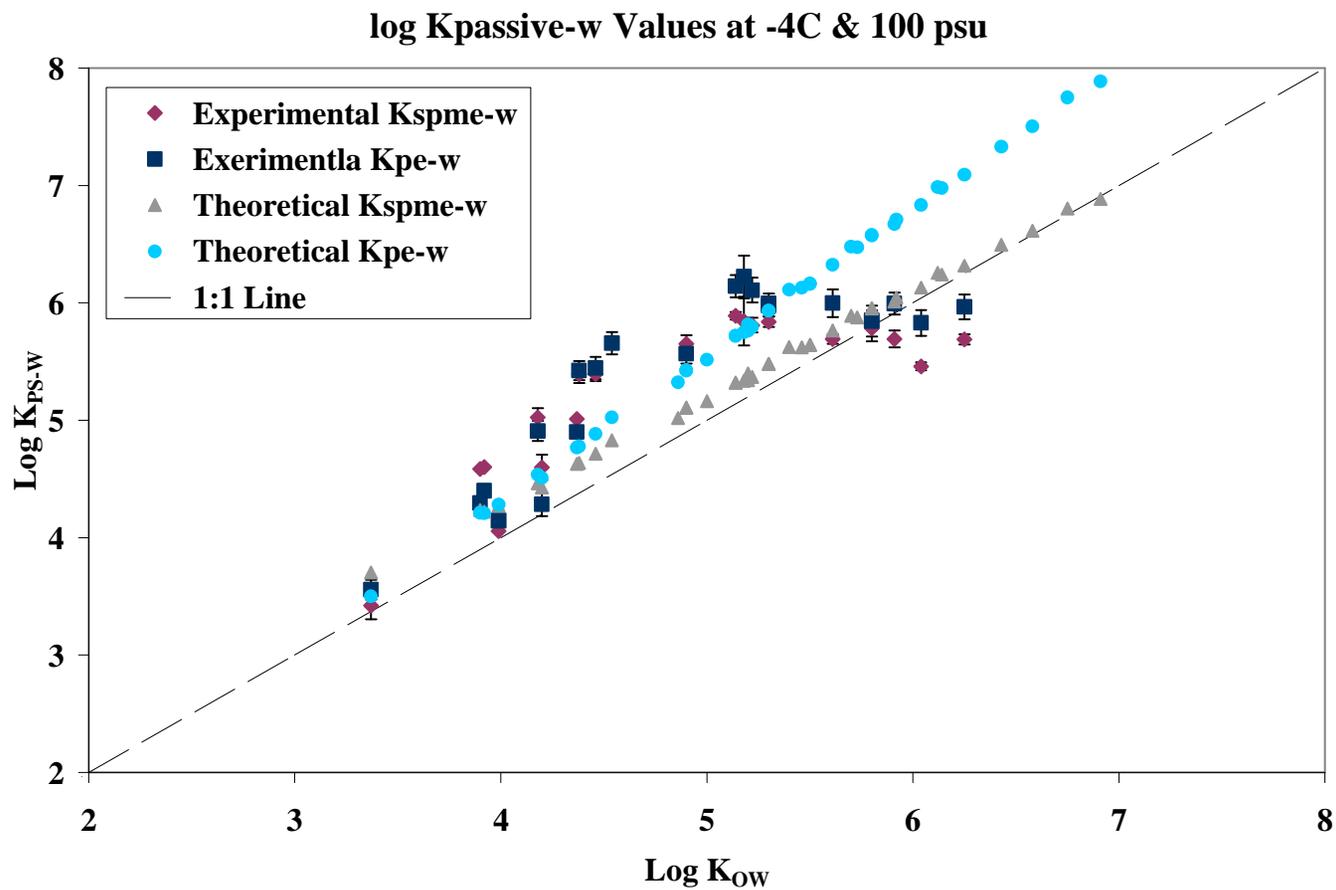
**Figure 16.** Averaged experimental  $K_{SPME-W}$  at 2 °C and salinities of 0 and 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.



**Figure 17.** Averaged experimental  $K_{PE-W}$  at 2 °C and salinities of 0 and 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.



**Figure 18.** Averaged experimentally derived  $K_{SPME}$  and  $K_{PE-W}$  at -4 °C and salinity 100 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.



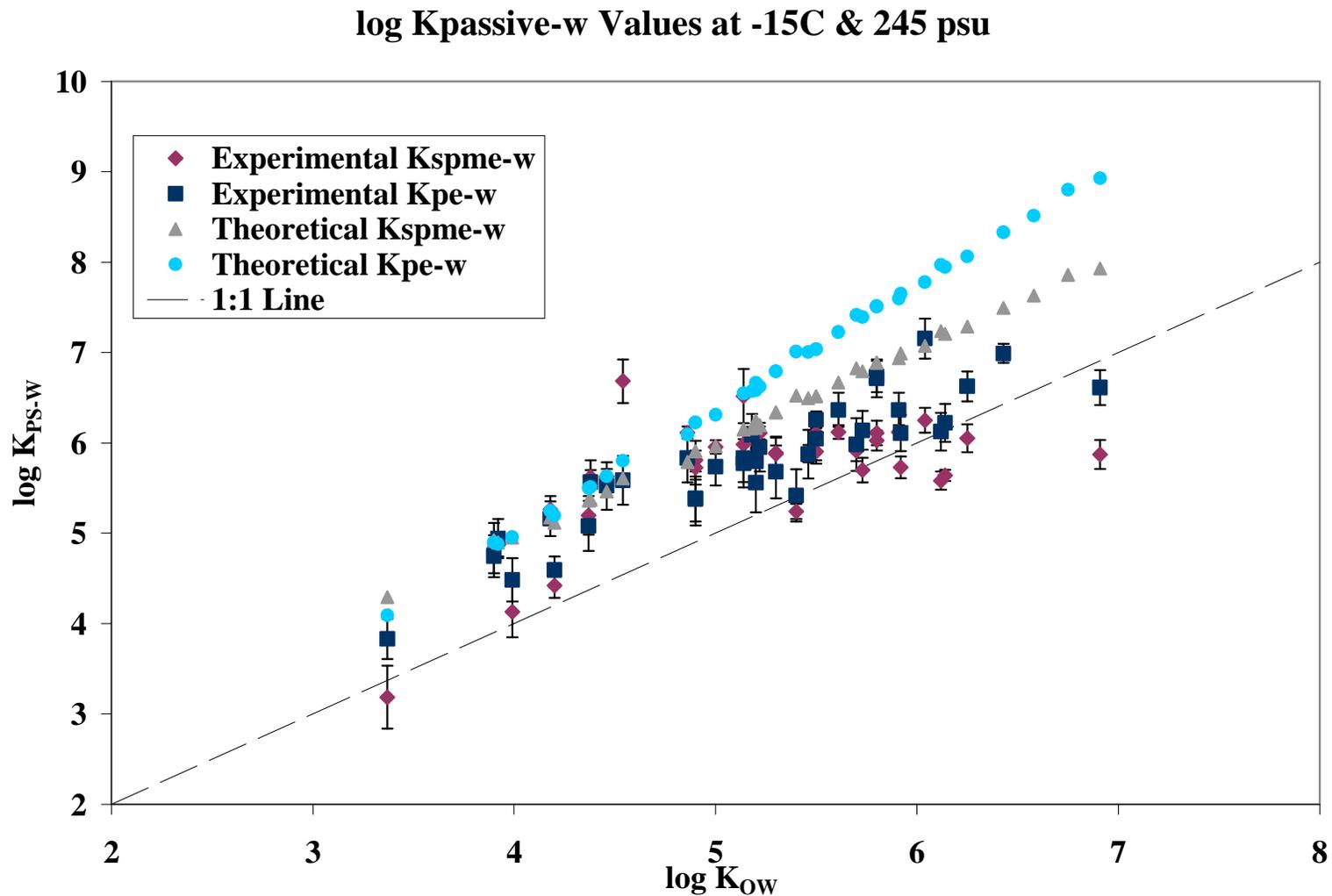
**Figure 19.** Averaged experimental  $K_{SPME-W}$  and  $K_{PE-W}$  at  $-4\text{ }^{\circ}\text{C}$  and a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.

with  $\log K_{OW}$  values above 5.5 leveled off with values near the theoretical  $\log K_{SPME-W}$  line for both SPME and PE samples. Though compounds with  $\log K_{OW}$  values above 5.5 do not fall on the linear line expected, they are much improved from the previous values and plot much higher than the 1 to 1 linear relationship between the  $\log K_{PS-W}$  and  $\log K_{OW}$  values displayed at standard conditions (Figure 19). These results show there is an obvious effect on the equilibrium partitioning coefficient at  $-4\text{ }^{\circ}\text{C}$  and 100 psu.

The final experiment was conducted at  $-15\text{ }^{\circ}\text{C}$  and 245 psu. The theoretical and experimental  $\log K_{PS-W}$  values for the  $-15\text{ }^{\circ}\text{C}$  experiment were calculated as previously mentioned. The water concentrations were used in the calculation of the  $K_{PS-W}$  and were checked against the calculated solubilities at  $-15\text{ }^{\circ}\text{C}$  at 245 psu and the water concentrations were all below compound solubility. In the  $-15\text{ }^{\circ}\text{C}$  experiment, the SPME samples displayed good replication, while there was some variation between the PE replicates however no replicates were excluded from results. In all of the SPME replicates and a few of the PE replicates, a few HMW PAH compounds indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were not detected in the passive samplers and therefore no  $K_{PS-W}$  could be calculated. As presented in the other experiments, in the initial results the SPME and PE experimental  $\log K_{PS-W}$  values increase with increasing  $\log K_{OW}$  until a value of 4.5. After a  $\log K_{OW}$  of 4.5 is reached, the experimental  $\log K_{PS-W}$  values begin to decrease as in the previous experiments (Figure 20). All compounds for both passive samplers are well below the expected theoretical lines. As in the  $-4\text{ }^{\circ}\text{C}$  experiment, the PRCs were used to correct the compounds for equilibrium. Corrections from PRCs greatly increase the values of the higher experimental  $\log K_{PS-W}$  values, displayed in the priority PAH and LMW compounds present in Staffjord oil. In the SPME and PE data sets, the majority of the compounds are still below the respective theoretical line, with the only exception being anthracene in the SPME data set (Figure 21). The anthracene data point for the SPMEs does not follow the trend of the remainder data, suggesting there was some complication in the extraction of the SPMEs or the water sample. The data was rechecked to ensure it was properly captured, however there was no explanation for this difference. Though these points fall below the expected theoretical lines, the majority of the compounds plot much higher than the 1 to 1 linear relationship between the  $\log K_{PS-W}$  and  $\log K_{OW}$  values displayed at standard conditions (Figure 21). These results show there is an obvious effect on the equilibrium partitioning coefficient at  $-15\text{ }^{\circ}\text{C}$  and 245 psu.

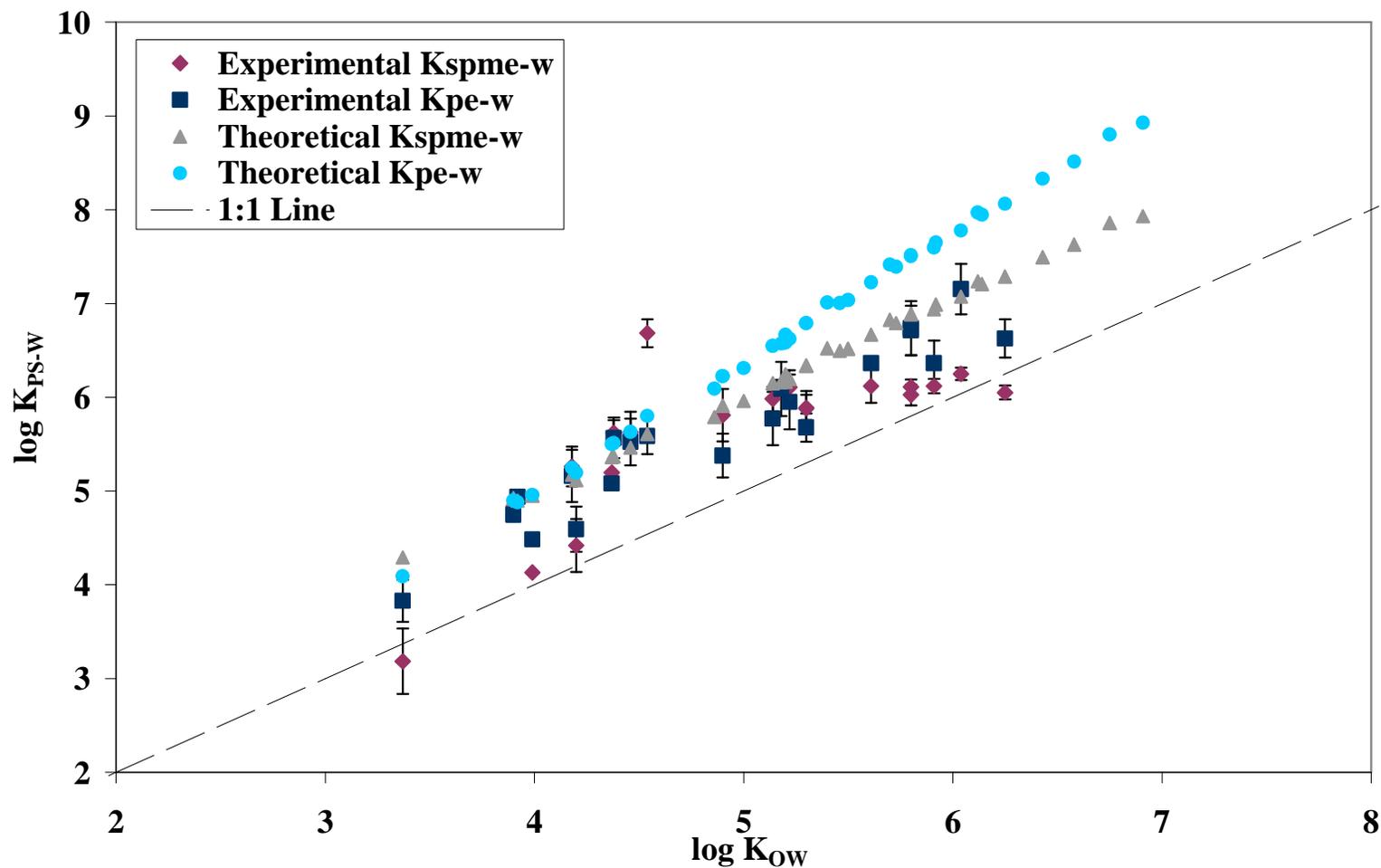
Analyzing the all of the experiments, the effect of salinity is evident. In the  $20\text{ }^{\circ}\text{C}$  experiment, the addition of 35 psu displays the greatest effect in the PE samples, though there seems to be a small effect evident in the SPME results (Figures 11 & 13). In the PE results, the majority of the 35 psu data points plot slightly above the corresponding 0 psu data points. In the  $2\text{ }^{\circ}\text{C}$  experiment, as expected, there is a greater increase in the experimental  $\log K_{PS-W}$  with the increase in the salinity from 0 psu to 100 psu (Figures 16 & 17). As in the  $20\text{ }^{\circ}\text{C}$  experiment, the salinity effect is larger in the PE samples than in the SPME samples. Overall, these samples display that salinity does effect the partitioning of compounds into passive samplers and must be accounted for with the Setschenow constant equation.

The temperature effect displayed in the experiments was opposite that found with the salinity effect. When 0 psu data from the  $20$  and  $2\text{ }^{\circ}\text{C}$  experiments are compared, there seems to be a more obvious effect in the SPME data, with the  $2\text{ }^{\circ}\text{C}$  data plotting above the  $20\text{ }^{\circ}\text{C}$  data points (Figures 22 & 23). An opposite trend is visible in the PE data set, with the  $20\text{ }^{\circ}\text{C}$  data points

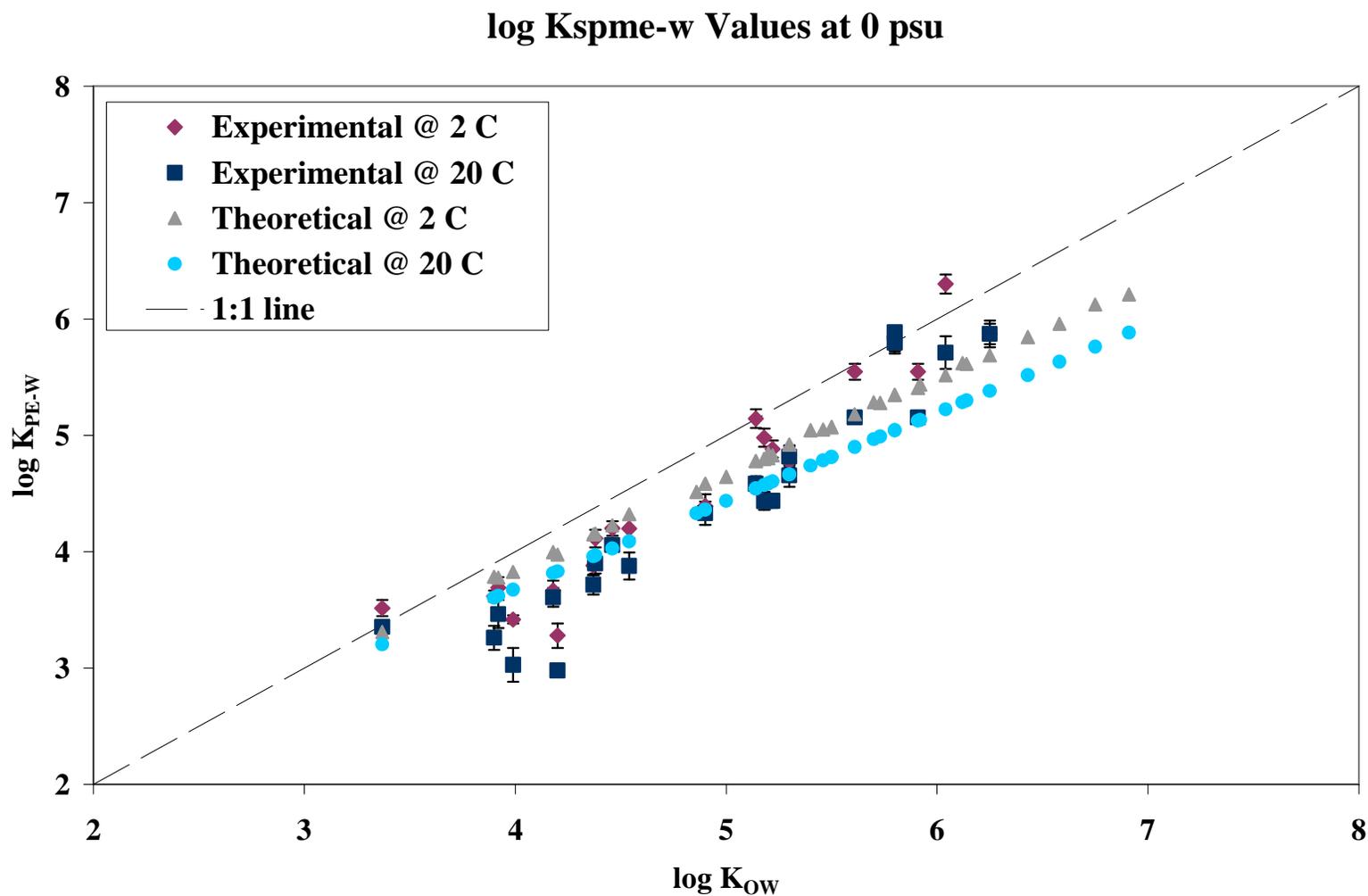


**Figure 20.** Averaged experimentally derived  $K_{SPME}$  and  $K_{PE-W}$  at -15 °C and a salinity 245 psu plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations. This figure incorporates all the PAH compounds included in Table 1.

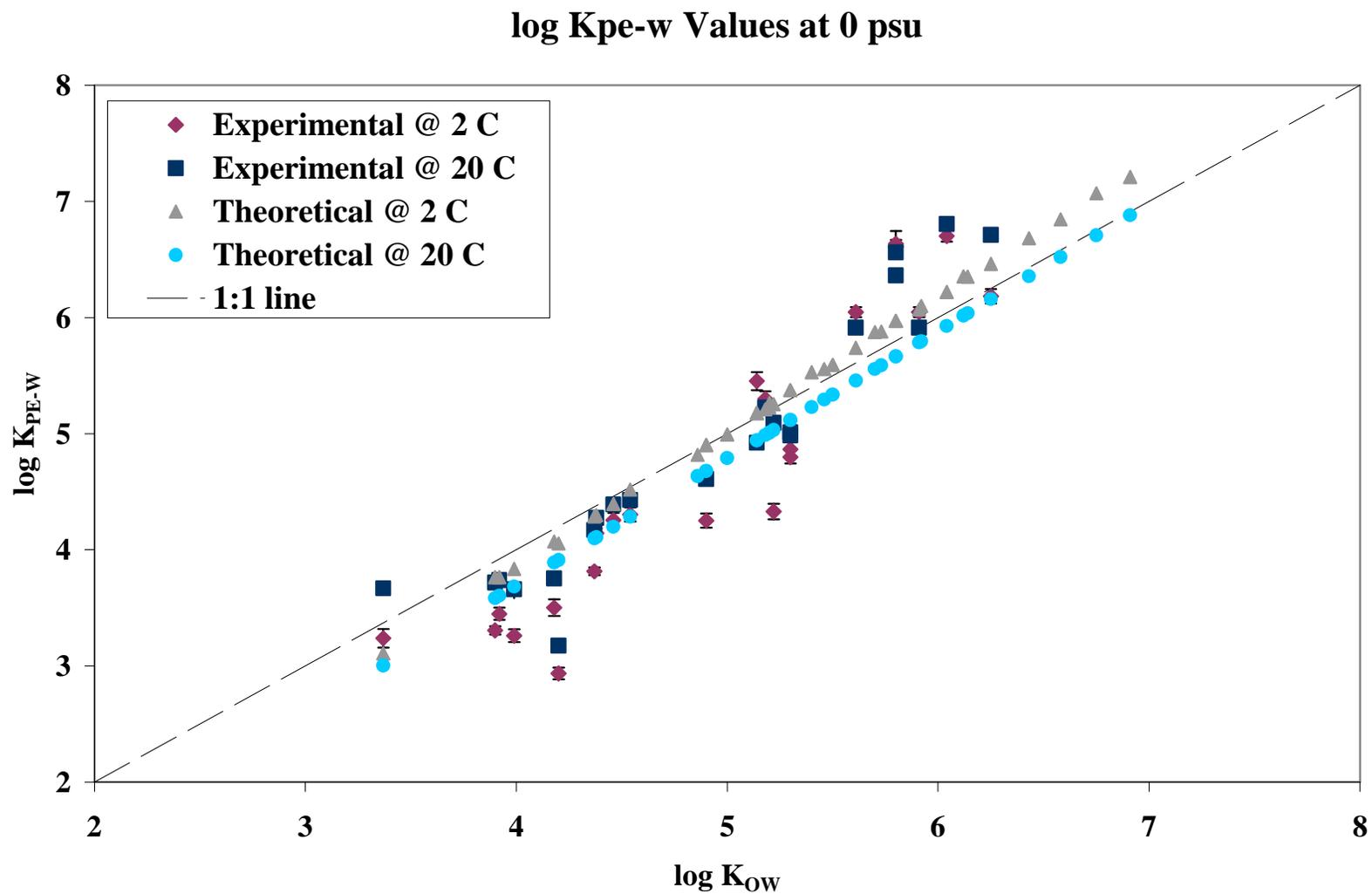
### log K<sub>ps-w</sub> Values at -15C & 245 psu



**Figure 21.** Averaged experimental  $K_{SPME-w}$  and  $K_{PE-w}$  at -15 °C and a salinity of 245 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.



**Figure 22.** Averaged experimental  $K_{SPME-W}$  at a salinity of 0 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.



**Figure 23.** Averaged experimental  $K_{pe-w}$  at a salinity of 0 psu, including only the priority PAHs and LMW compounds present in the Stafford crude oil, to demonstrate the effect of temperature. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.

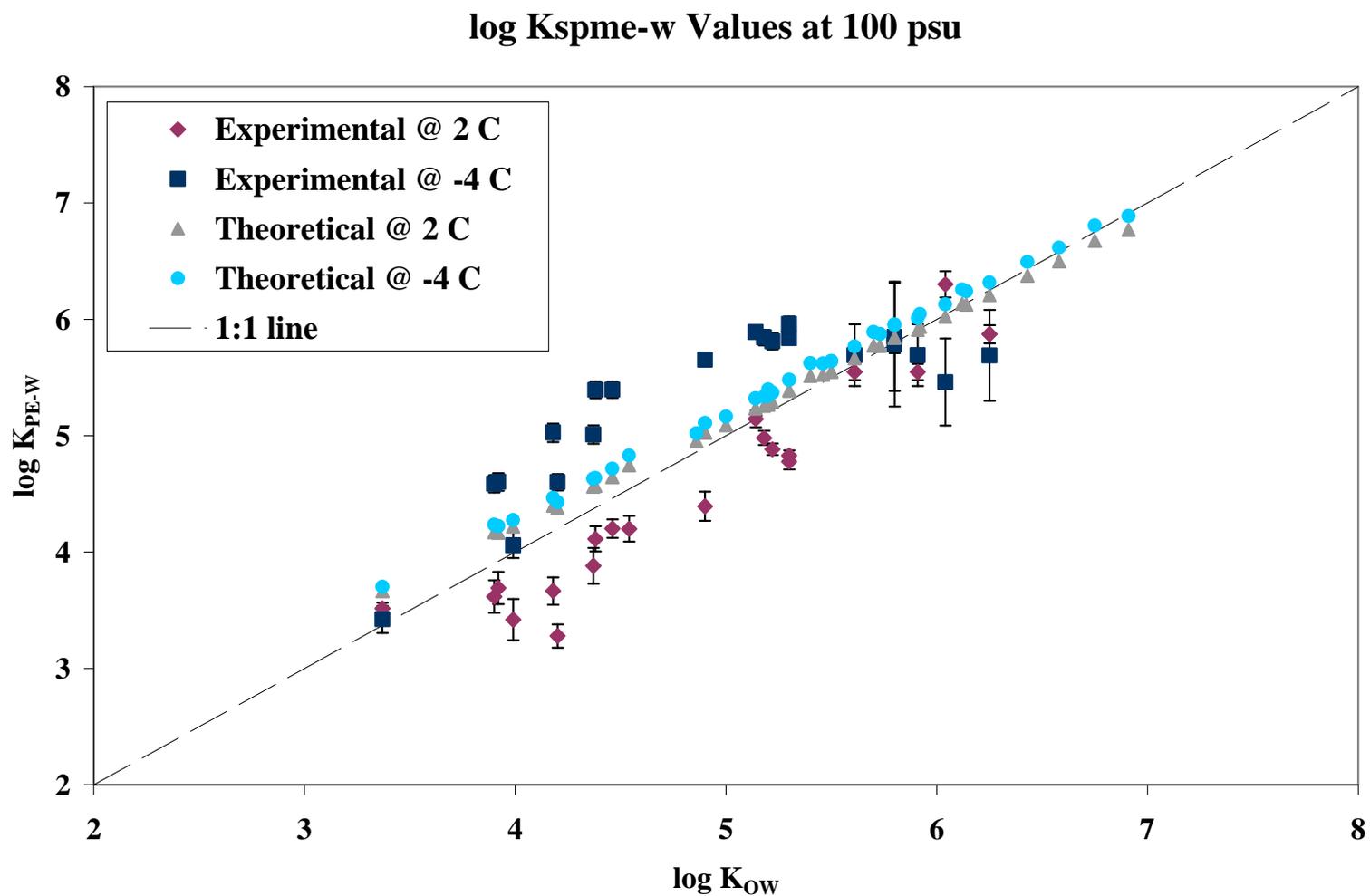
being slightly greater than the 2 °C data points; however the trend is not as strong as in the SPME data set. Though a smaller temperature difference was present between the 2 and -4 °C experiments than the 20 and 2 °C experiments, there was a much larger difference between experimental log  $K_{PS-W}$  values in the 2 and -4 °C experiments for both the SPME and PE samples than in the 20 and 2 °C experiments (Figures 24 & 25). In both the SPME and PE data sets, there was not as much difference between the samples in the compounds with log  $K_{OW}$  values over 5.5. In fact in the PE samples, the opposite temperature effect was visible for these few compounds. However, this is most likely an effect of non-equilibrium, than the effect of temperature. Though there is some contradiction in a few of the data points, the overall visible trend is as the temperature decreases, the equilibrium partitioning coefficients increase. This increase gets even larger the lower the temperature gets from standard conditions.

Though further investigation is needed for the compounds with log  $K_{OW}$  values above 5, we are confident that the data from this study presents accurate log  $K_{PS-W}$  values for the compounds with log  $K_{OW}$  values below the value of 5. It is these compounds that more readily dissolve into the water column and are usually present at higher concentrations in the water column after an oil spill event. This makes these compounds more bioavailable and potentially more toxic to organisms and makes them of higher importance in investigating the fate and transport of PAHs in the Arctic environment.

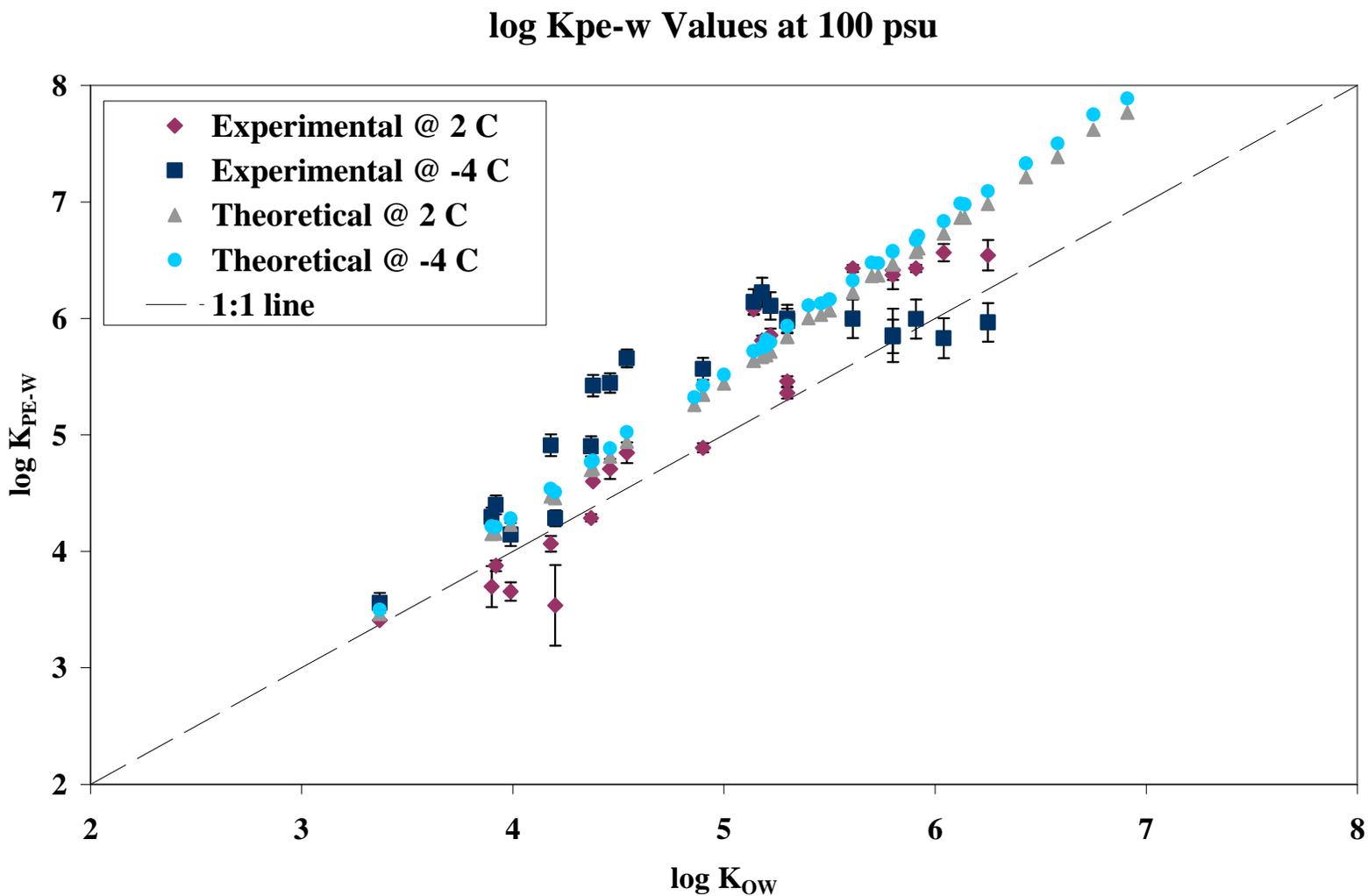
Crude Oil Study. Three replicates of the WSF of Statfjord oil were prepared and analyzed by liquid-liquid extraction. The WSF for Statfjord crude oil was composed mainly of LMW compounds, such as phenolic compounds, naphthalenes and methylated-naphthalenes, which were similar to reports from previous studies (Table 7; Faksness et al. 2008). Other compounds with notable concentrations were fluorene, methyl-fluorene, dibenzothiophene, phenanthrene, and methyl-phenanthrene. Very few HMW compounds (< 200) were present in the WSF of the Statfjord crude oil, again similar to other findings (Table 7; Faksness et al. 2008). Due to their high abundance in the WSF, the compounds listed above will be the focus in the remainder of this discussion.

After the passive samplers were analyzed, PAH concentrations in the sampler were converted to concentrations present in the water with equation 1. The experimental derived  $K_{PS-W}$  values at 2 °C and 0 psu adjusted for equilibrium with the PRCs and corrected with the derived Setschenow constants to reflect the salinity of the Narragansett Bay water used in the study (30 psu) was utilized for this calculation since it most closely resembled the conditions present for this laboratory experiment. The sampler derived water concentrations were then compared to the extracted water concentrations of the WSF.

After discussion with colleagues, it was discovered that even though the water was treated with biocide there was potential over longer term experiments for bacteria to re-grow after the initial biocide treatment and potentially biodegrade the PAHs changing the composition of the WSF sample (Odd Gunnar Bradsted, SINTEF, personal communication). To ensure that there was no bacterial degradation of oil during the experiment, two time periods were selected, three and four weeks, for comparison of concentrations over time. There appeared to be no change in sampler concentration with time for the prevalent PAHs, so it was concluded that significant bacterial degradation did not significantly affect our results during this period. There was little variation between replicates, so no replicates were excluded from averaging.



**Figure 24.** Averaged experimental  $K_{SPME-W}$  at a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Statfjord crude oil, to demonstrate the effect of temperature. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.



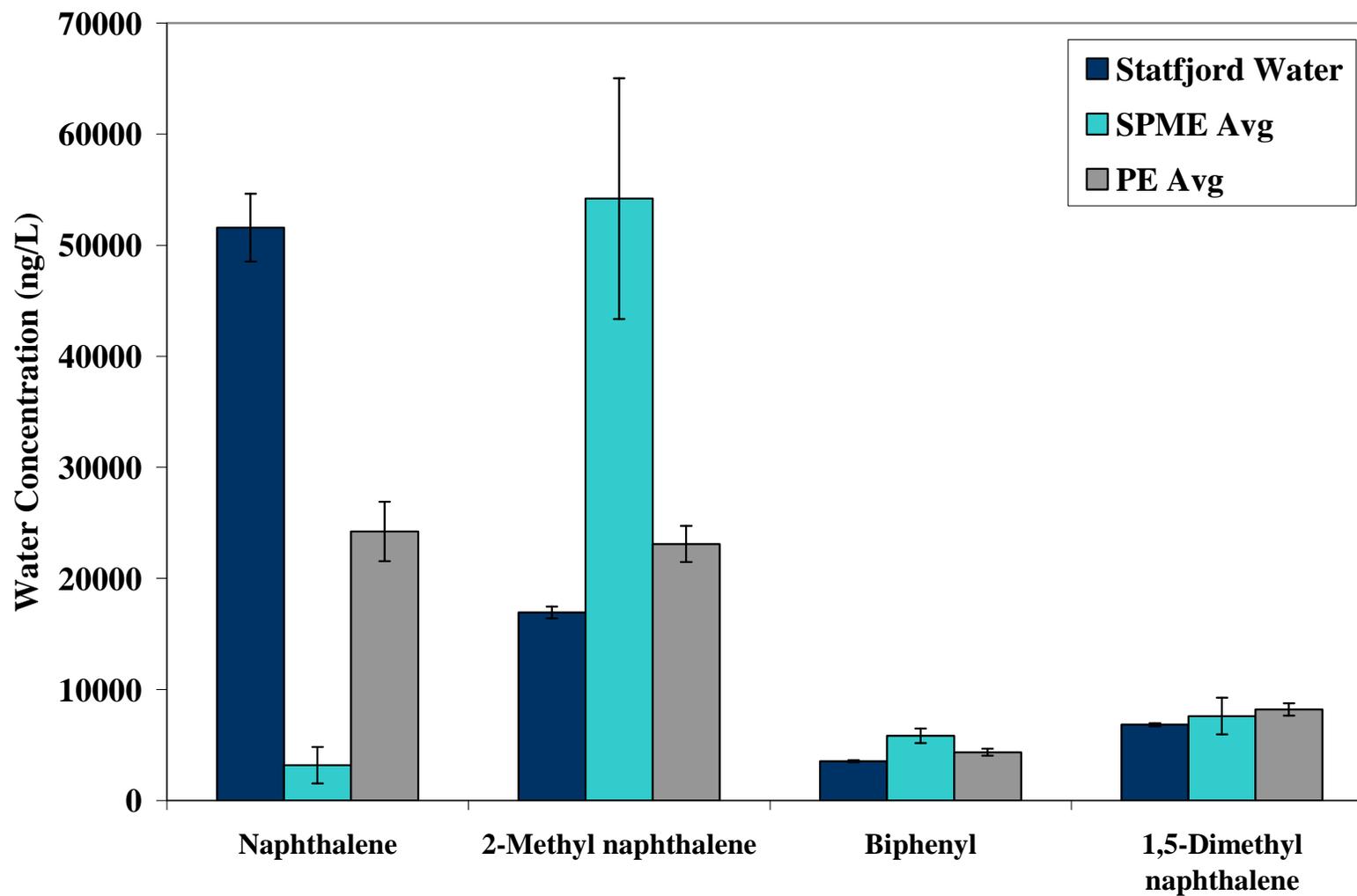
**Figure 25.** Averaged experimental  $K_{PE-W}$  at a salinity of 100 psu, including only the priority PAHs and LMW compounds present in the Stafford crude oil, to demonstrate the effect of temperature. The experimental data points are plotted with the theoretically calculated equilibrium partitioning coefficients using the van't Hoff and Setschenow equations.

**Table 7.** Composition of PAHs in the WSF of Statfjord crude oil

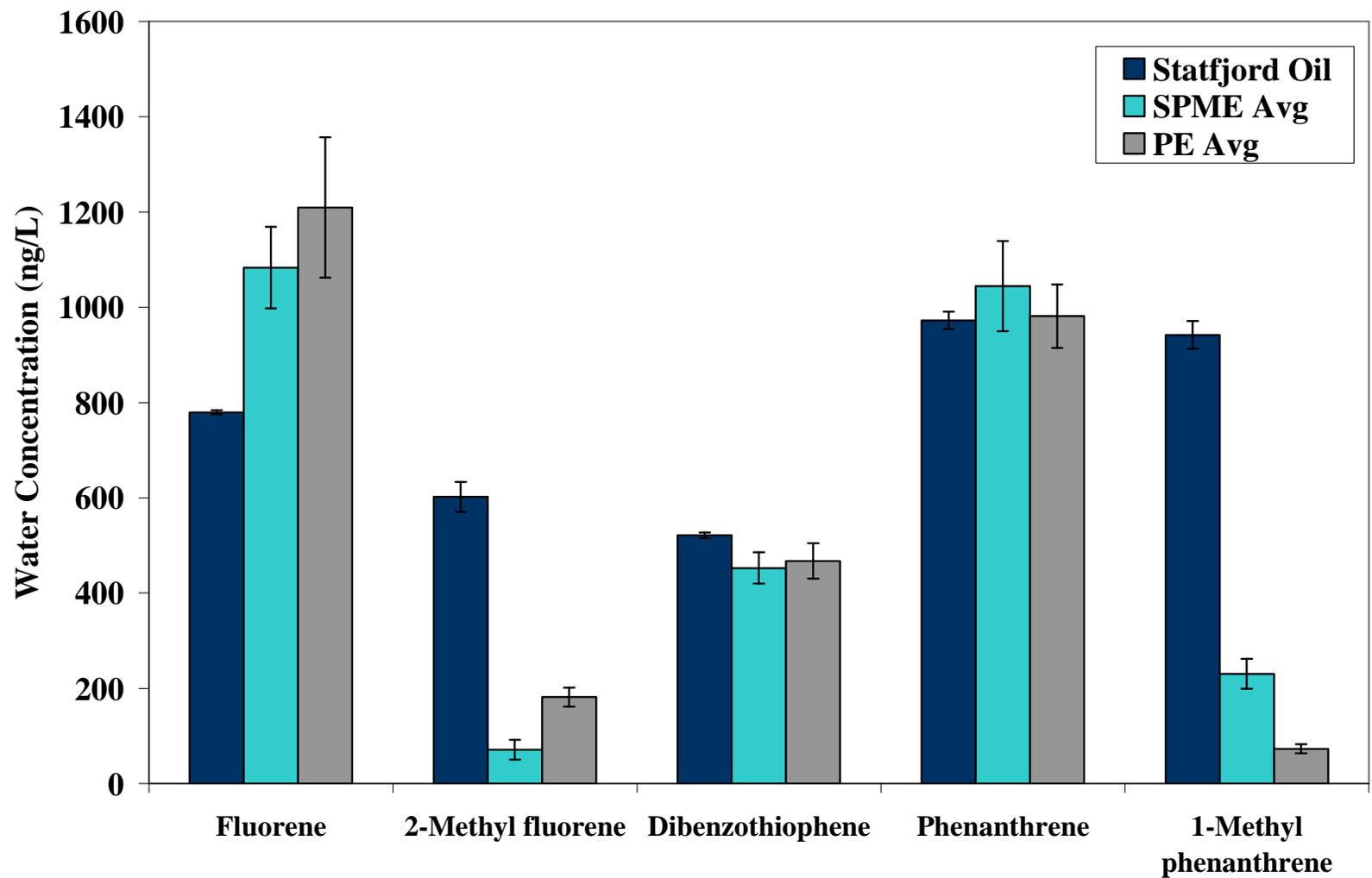
<b>Standards</b>	<b>Average (ng/L)</b>	<b>Standrd deviation</b>
p-Cresol	19267.08	892.96
m-Cresol	15762.24	884.83
o-Ethyl phenol	3190.93	42.22
p-Ethyl phenol	10268.64	1253.80
m-Ethyl phenol	11336.38	1617.43
2,3-Dimethyl phenol	2024.70	1075.76
Naphthalene	51581.22	3047.29
3,4-Dimethyl phenol	10942.73	440.93
2,4,6-Trimethyl phenol	4838.48	936.24
2,3,5-Trimethyl phenol	3343.41	428.62
2-Methyl naphthalene	16922.90	525.61
2,3,5,6-Tetramethyl phenol	4256.10	698.67
Biphenyl	3524.99	78.67
1,5-Dimethyl naphthalene	6826.42	143.83
Acenaphthylene	82.75	2.70
2-isopropyl naphthalene	69.84	2.06
Acenaphthene	103.57	1.03
2,3,5-Trimethyl naphthalene	707.10	18.87
Fluorene	779.23	4.40
9-Ethyl fluorene	98.70	15.67
1,4,6,7-Tetramethyl naphthalene	104.59	24.72
2-Methyl fluorene	602.14	31.43
2,6-Diisopropyl naphthalene	8.55	2.17
1,2,5,6-Tetramethyl naphthalene	431.77	423.26
Dibenzothiophene	521.67	5.66
9-n-Propyl fluorene	55.59	1.70
Phenanthrene	972.29	18.24
Anthracene	101.02	2.47
2-Methyl Dibenzothiophene	225.51	21.99
4,5-Methylene phenanthrene	18.99	1.28
1-Methyl phenanthrene	941.98	29.03
9-Methyl anthracene	44.46	2.51
3,6-Dimethyl phenanthrene	61.91	4.09
1,2-Dimethyl dibenzothiophene	348.50	65.99
Fluoranthene	4.11	0.31
2,4,7-Trimethyl dibenzothiophene	63.69	13.69
Pyrene	3.49	2.75
1,2,5/1,2,7-Trimethyl phenanthrene	39.77	5.20
Retene	9.87	6.27
1-Methyl pyrene	2.97	1.58
Chrysene	12.16	1.98
Benz(a)anthracene	17.64	3.42
1-Methyl chrysene	18.01	4.27
Benzo(b)fluoranthene	0.40	0.12
7,12-Dimethyl benz(a)anthracene	13.57	0.95
Benzo(h)fluoranthene	0.39	0.35
Benzo[a]pyrene	0.59	0.04
Perylene	0.58	0.24
Indeno(1,2,3-c,d)pyrene	0.00	0.00
Dibenzo(a,h)anthracene	0.00	0.00
Benzo(g,h,i)perylene	0.97	1.68

The SPME and PE average water derived concentration was compared to the extracted WSF concentration. Overall there was relative agreement between the passive samplers, as well as with the extracted water concentrations, suggesting either sampler would be suitable to use in oil spill conditions. With the exception of naphthalene, PEs and SPMEs predicted the water samples concentration within a factor of two or better for the majority of compounds present in the WSF samples. Since concentrations in the natural environment are not static due to factors such as currents, changing tides, losses to the atmosphere, etc., a snapshot sample taken cannot be representative of passive sampler exposure. Additionally, conventional extraction methods of total water concentrations by definition will tend to over-estimate the dissolved concentration in the environment. Thus, we consider an agreement within a factor of two between passive samplers and conventional methods to be an acceptable standard. This agreement demonstrates passive samplers can be a valuable tool in oil spill monitoring and damage assessments.

The greatest difference between the passive sampler and extracted water concentration ( $52,000 \text{ ng}\cdot\text{L}^{-1}$ ) was present for naphthalene, with the SPME average concentration ( $3,200 \text{ ng}\cdot\text{L}^{-1}$ ) an order of magnitude lower than the water concentration (Figure 26). The PE reflected water concentration ( $24,000 \text{ ng}\cdot\text{L}^{-1}$ ) was little less than half of the WSF water concentration ( $52,000 \text{ ng}\cdot\text{L}^{-1}$ ). The noticeable difference between the samplers could be due to loss during the experiment, due to the shaking of the samples and the volatility of naphthalene. The water samples were not agitated during the experiment as the PE and SPME samples were decreasing the potential for loss of naphthalene during the experiment. There was also a large difference in the methyl-naphthalene concentrations between the SPME concentration ( $54,000 \text{ ng}\cdot\text{L}^{-1}$ ) and the other two samples ( $17,000 \text{ ng}\cdot\text{L}^{-1}$  WSF and  $23,000 \text{ ng}\cdot\text{L}^{-1}$  PE). The large difference between the SPME samples and the other two could have been from sample contamination during extraction, since PE and WSF water sample concentrations display similar concentrations of methyl-naphthalene. Biphenyl and dimethyl-naphthalene were prominent in the composition of the WSF. Both passive samplers displayed similar concentrations for each of these compounds, and were in close agreement with the WSF water concentration. This also occurred for dibenzothiophene and phenanthrene (Figure 27). For methyl-fluorene and methyl-phenanthrene, the water concentration was greater than reflected by the passive samplers. For methyl-fluorene, the sampler concentrations show relative agreement (SPME  $71 \text{ ng}\cdot\text{L}^{-1}$ ; PE  $180 \text{ ng}\cdot\text{L}^{-1}$ ), while for methyl-phenanthrene there is a greater difference in the concentration reflected by the samplers (SPME  $230 \text{ ng}\cdot\text{L}^{-1}$  and PE  $72 \text{ ng}\cdot\text{L}^{-1}$ ). For fluorene, the opposite trend was visible, with the passive samplers displaying a larger concentration than found in the WSF water (Figure 27). Though there was a slight difference in concentrations between the samplers and the water, there was very little difference between the passive sampler concentrations, suggesting the liquid-liquid extraction of the water sample was not able to recover all of the fluorene from the water sample. For the most part, the passive samplers were able to predict PAH concentration present in the water samples, with the exception of the most volatile PAHs (possibly due to losses during analysis) (Figures 26 & 27). The underestimation of the methyl-fluorene and -phenanthrene by the passive samplers implies there could be complications in assessing equilibrium concentrations for the methylated compounds. Perhaps using a methylated PRC for this investigation could have better represented the kinetics of the methylated compounds in the passive samplers. Overall there was relative agreement between the passive samplers, as well as with the extracted water concentrations, suggests either sampler would be suitable to use in oil spill conditions.



**Figure 26.** Averaged water concentrations from liquid-liquid extraction of Statfjord water samples compared to SPME and PE derived water concentrations a few LMW PAH compounds.



**Figure 27.** Averaged water concentrations from liquid-liquid extraction of Statfjord water samples compared to SPME and PE derived water concentrations a few LMW PAH compounds.

*Field Deployment.* The passive samplers were deployed in Narragansett Bay from March 26, 2009 until April 17, 2009. During the entire deployment, temperature ranged from 3.78 °C to 8.55 °C and salinity ranged from 28.22 psu to 32.07 psu. PEs were deployed for the entire deployment, however there were complications with the SPME deployment. Since there were only four copper housing for the SPMEs, upon recovery, the housing had to be opened and

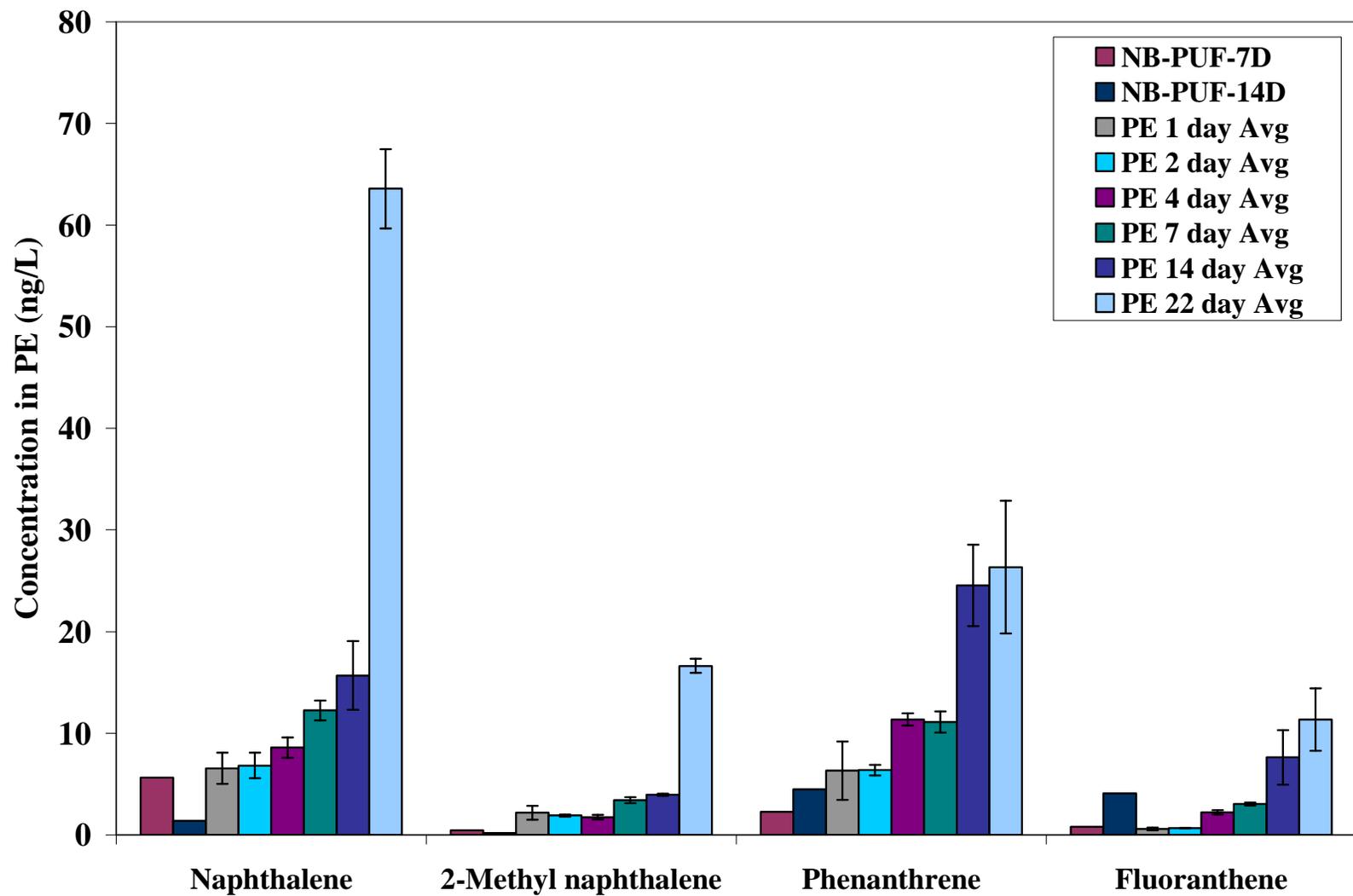
SPMEs individually removed. While in the laboratory, this is not difficult, in the field, however there were complications and some SPMEs were lost during the recovery. The loss of the SPME fibers was so great that there were only enough SPMEs to complete a 14 day field deployment. A more suitable set-up would have been to have a copper housing for each deployment period to minimize the loss of SPMEs in the field. No PEs were lost during the deployment, so a full 22 day deployment was performed.

Another complication occurred during the deployment. The contamination of field blanks of both SPMEs and PEs exceeded the concentration of field samples. For the PEs, the majority of the contamination occurred in the day 1 field blank. In the SPME field samples, the greatest PAH concentration in the field blanks also occurred on day 1, however contamination of field blanks above field samples was a problem throughout the deployment. The small sample size also added to the field blank complication. Similar compounds were found in the field blanks of both the SPMEs and the PEs. The agreement in the contamination of the samplers suggests that it was not laboratory contamination; rather this contamination was reflective of the air concentration present at the time of recovery on day 1.

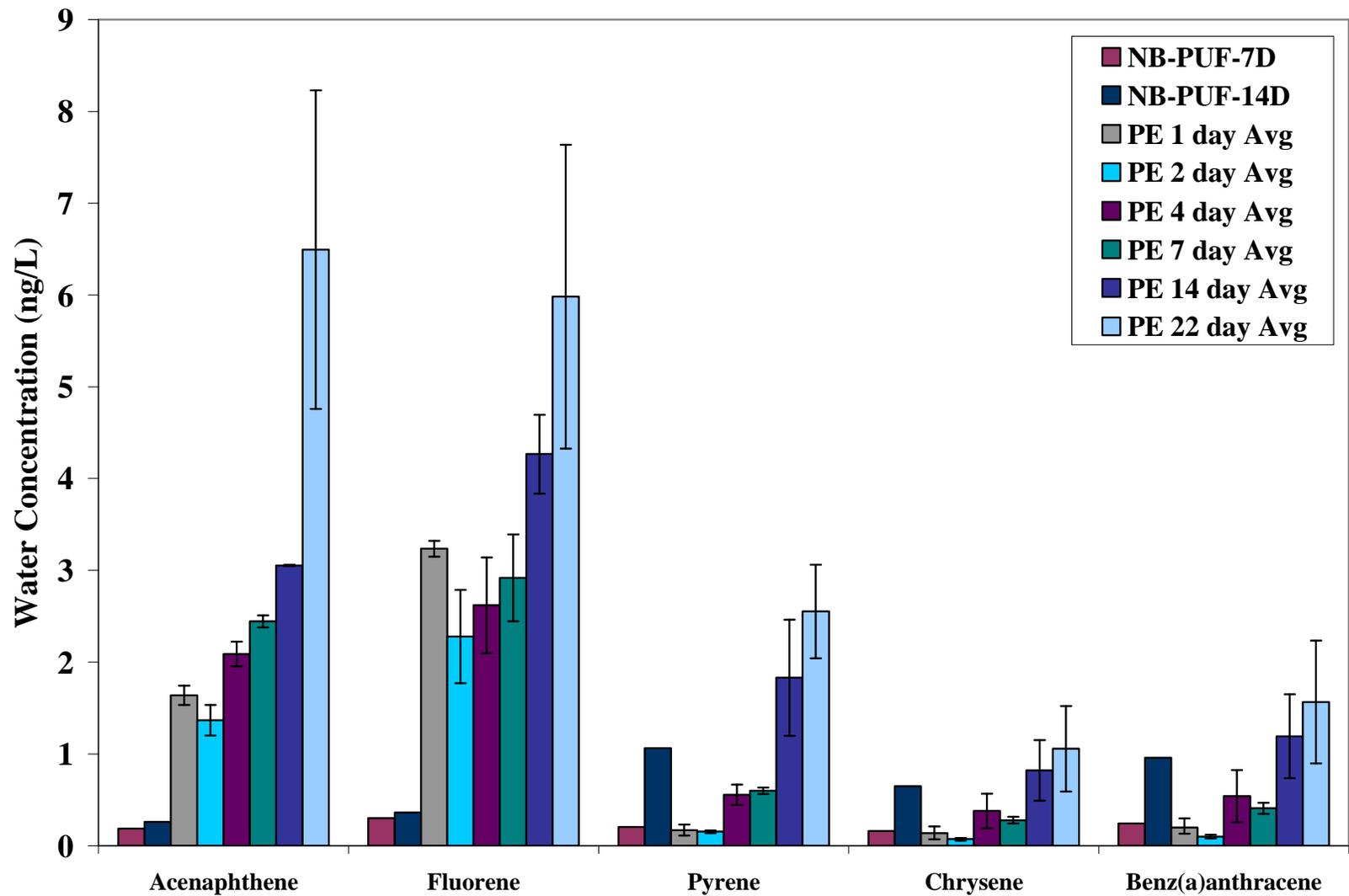
The PUF results reflect the dissolved water concentration present on the deployment day sampled (Figures 28 & 29). Two days were sampled over the deployment period to reflect possible changes in the water concentration during the deployment period (days 7 and 14). The day 14 concentrations are consistently higher than those on day 7 for all compounds except for naphthalene and methyl-naphthalene (Figure 28). It is possible that there was an event that released PAHs after day 7 such as atmospheric deposition, release from the sediment, ship traffic or a weather event.

After the passive samplers were analyzed, PAH concentrations in the sampler were converted to concentrations present in the water with equation 1. Similar to the WSF data analysis, the experimental  $\log K_{PS-W}$  values determined in the 2 °C at 0 psu were adjusted for equilibrium with the PRCs and corrected with the derived Setschenow constants to reflect the salinity of Narragansett Bay (30 psu) and utilized for this calculation since it most closely resembled the conditions present for the experiment. The loss rates were also recalculated to match the partition coefficients. The sampler derived water concentrations were then compared to the PUF water concentrations (Figures 28 & 29).

When the SPME results are compared to the PUF results, benzo[a]pyrene is the only compound detected where no blank concentration exceeded field concentrations. Benzo[a]pyrene PUF concentrations on day 7 are similar to the SPME concentrations on all days. The SPME concentrations are lowest on day 14 and do not reflect the higher concentrations present in the water column that day. Using only benzo[a]pyrene, SPMEs demonstrated they could reliably reflect the water column concentration. This deployment served as a learning experience for deploying SPMEs in the field. In future deployments these problems can be overcome through a



**Figure 28.** Averaged water concentrations from active sampling of Narragansett Bay compared to SPME and PE derived water concentrations a few LMW PAH compounds.



**Figure 29.** Averaged water concentrations from active sampling of Narragansett Bay compared to SPME and PE derived water concentrations a few LMW PAH compounds.

copper housing being deployed for each sampling period and a larger volume of SPMEs deployed for each sample replicate. A larger volume can be achieved through deploying longer SPME replicates or purchasing SPME fibers which are composed of a thicker PDMS coating.

The larger volumes of PE samples were able to accumulate more PAH compounds. More compounds were detected in the PE samples than those presented in the figures, however only the prominent PAHs are displayed (Figure 28 & 29). The PE concentrations were highest on day 22 for all PAH presented, which mirrors the PUF water concentrations. For naphthalene and methyl-naphthalene, the 1, 2, and 4 day samples were similar to the 7 day PUF sample. In the 14 day PUF concentrations, there is a decrease in naphthalene and methyl-naphthalene (Figure 28). This decrease is not exhibited in the PE results for either compound, where the concentration continues to increase. Fluoranthene, pyrene, chrysene and benzo(a)anthracene all display a similar pattern (Figure 29). For all of these compounds, the 1 and 2 day PE samples are similar to the 7 day PUF water samples. The 4, 7, 14 and 22 day concentrations of these compounds are higher than the 1 and 2 day concentrations, with the 22 day concentrations are the highest. Phenanthrene also resembles this trend. Acenaphthene and fluorene concentrations of the PEs were both higher than the PUF water concentrations on all days; however, their concentrations increased in the day 14 and 22 samples similar to the other compounds. This suggests that there was an increase in PAHs over the deployment with a larger release after day 7, which is captured in the 14 and 22 day samples (Figure 28 & 29). From previous work, it is known that PE samplers equilibrate for the lower molecular weight PAHs (such as acenaphthene and fluorene) in a matter of several days in Narragansett Bay. Thus, changes in the accumulation of these PAHs in passive samplers over time likely reflect increasing dissolved concentrations. In contrast, the higher molecular weight compounds, with their increased equilibrium time, would not have sufficient time to reflect this increase. As mentioned previously, it is possible that there was an event that released PAHs after day 7 such as atmospheric deposition, release from the sediment, ship traffic or a weather event.

During this deployment, PEs were hardy enough to withstand the stress of the environment, yet were capable of reflecting an increase of PAHs in the bay. The deployment in Narragansett Bay demonstrated SPMEs and PEs were capable to reflect dissolved PAHs water concentrations accurately, though PEs are a more valuable tool at consistently capturing background concentrations of PAHs present in the environment.

*Conclusions.* This study commenced to examine the effect of temperature and salinity on the equilibrium partitioning coefficients of passive samplers, so they may be an effective tool at investigating the fate and transport of oil, specifically PAHs, in the Arctic environment. Time constraints linked to the simultaneous analysis of phenols and PAHs by GC-MS prevented us from studying the uptake of phenols by passive samplers. We note, however, that other studies have shown passives samplers, such as PE, are capable to reliably predict water concentrations of polar compounds (e.g., Sacks 2010). For the PAHs investigated, it was expected the equilibrium partitioning coefficients would increase with decreasing temperature and increasing salinity. The combination of the decreasing temperature and increasing salinity is substantial in the Arctic environment and possesses a potential complication when utilizing passive samplers. This study was able to reliably demonstrate that the extreme temperature and salinity conditions that passive samplers would face in the Arctic environment do have a significant effect on the partitioning of compounds into passive samplers. Both temperature and salinity must be accounted for when

deploying passive samplers in this unique environment (Tables 8 & 9). Another effect of this harsh environment when deploying passive samplers is allowing sufficient time for the passive samplers to reach equilibrium, especially for the higher molecular weight compounds. PRCs can be employed to reflect equilibrium concentrations; however, a more diverse mixture of PRCs maybe needed in the Arctic environment to address the equilibrium time of the higher molecular weight compounds and the methylated compounds. Through the crude oil study, as well as the field deployment, these passive samplers have revealed they are able to be deployed either during an oil spill event or prior an oil spill to study background concentrations and can accurately reflect the PAH concentrations present in the water column. The PE passive samplers were able to avoid complications in experiments and with their larger volume can more readily be deployed to determine background concentrations. The SPMEs and PEs can be deployed to represent time averaged concentrations, representing more accurate environmental concentrations, averaging out incorrect extreme concentrations that could be captured with discrete sampling. Because of this unique time averaged sampling, they may be useful to determine concentrations after an oil spill event. They are a valuable resource in studying the fate and transport of oil in ice, and with the completion of this study are now able to be used reliably.

## **5.0 Discussion of Importance to Oil Spill Response/Restoration**

The developed PE and SPME samplers will enable the oil spill community to deploy passive samplers as equilibrium devices to measure baseline conditions before a spill, as kinetic samplers during a spill and during the recovery phase of the natural ecosystem. Ice column testing will determine over what periods of time SPME and PE samplers need to be deployed.

PE and SPME samplers are cheap and can be easily deployed off any existing buoy. It is suggested that the required deployment time will be on the order of several days for the kinetic samplers. SPME samplers excel as kinetic samplers for short-time deployments. PE samplers can also be used to detect baseline values, or as a routine monitoring tool in areas where oil spills are common threats, such as harbors.

## **6.0 Technology Transfer**

The developed product is fully transferable from one cold region to another. The kinetics of water soluble compounds uptake depend mostly on temperature and currents. It will be operational in either salt- or freshwater. Increased saltiness of the water results in an increased partitioning to the passive samplers, which can be accounted for. In marked difference to the availability and comparability of benthic species, the results from PE and SPME samplers are easily comparable from one region to another. The deployment of passive samplers does not differ from one cold region to another. Everywhere, they have to be deployed off buoys for measurements of dissolved concentrations in the water column, or buried in ice or brine channels.

At this stage, SPME samplers have been transferred to collaborators at SINTEF and at UNH; in both cases the samplers are being used to better understand the fate of oil.

**Table 8.** List of experimental log  $K_{SPME-W}$  values determined in this study for the priority PAHs and LMW compounds present in the Statfjord crude oil

Compounds	log $k_{ow}$	log $K_{spme-w}$					
		20C @ 0psu	20C @ 35psu	2C @ 0psu	2C @ 100psu	-4C @ 100psu	-15C @ 245psu
Naphthalene	3.37	3.35 ± 0.03	3.36 ± 0.04	3.52 ± 0.07	3.51 ± 0.05	3.42 ± 0.12	3.18 ± 0.35
2-Methyl naphthalene	3.99	3.03 ± 0.15	3.13 ± 0.24	3.42 ± 0.04	3.63 ± 0.18	4.06 ± 0.11	4.13 ± 0.28
Biphenyl	3.9	3.26 ± 0.10	3.26 ± 0.17	3.62 ± 0.05	3.90 ± 0.14	4.59 ± 0.07	4.83 ± 0.28
1,5-Dimethyl naphthalene	4.37	3.72 ± 0.08	3.74 ± 0.10	3.88 ± 0.08	4.20 ± 0.15	5.01 ± 0.08	5.20 ± 0.21
Acenaphthylene	4.2	2.98 ± 0.03	2.96 ± 0.09	3.28 ± 0.11	3.63 ± 0.10	4.60 ± 0.07	4.42 ± 0.13
Acenaphthene	3.92	3.46 ± 0.12	3.56 ± 0.03	3.69 ± 0.09	4.04 ± 0.14	4.60 ± 0.08	4.88 ± 0.14
2,3,5-Trimethyl naphthalene	4.9	4.33 ± 0.10	4.33 ± 0.07	4.39 ± 0.10	4.84 ± 0.12	5.65 ± 0.06	5.81 ± 0.21
Fluorene	4.18	3.61 ± 0.08	3.70 ± 0.07	3.66 ± 0.09	4.03 ± 0.12	5.03 ± 0.08	5.26 ± 0.15
1,4,6,7-Tetramethyl naphthalene	5.3	4.66 ± 0.10	4.65 ± 0.07	4.83 ± 0.08	5.28 ± 0.05	5.96 ± 0.06	5.89 ± 0.18
1,2,5,6-Tetramethyl naphthalene	5.3	4.82 ± 0.09	4.80 ± 0.04	4.78 ± 0.10	5.09 ± 0.07	5.84 ± 0.04	5.88 ± 0.18
Dibenzothiophene	4.38	3.90 ± 0.09	3.91 ± 0.01	4.11 ± 0.08	4.48 ± 0.11	5.39 ± 0.07	5.62 ± 0.08
Phenanthrene	4.46	4.06 ± 0.04	3.29 ± 0.10	4.20 ± 0.06	3.85 ± 0.08	5.39 ± 0.07	5.63 ± 0.08
Anthracene	4.54	3.88 ± 0.12	4.20 ± 0.08	4.20 ± 0.08	4.65 ± 0.11	5.07 ± 0.17	6.68 ± 0.24
1-Methyl phenanthrene	5.14	4.58 ± 0.07	4.59 ± 0.02	5.14 ± 0.08	5.50 ± 0.07	5.89 ± 0.03	5.98 ± 0.11
Fluoranthene	5.22	4.44 ± 0.06	4.41 ± 0.03	4.88 ± 0.07	5.20 ± 0.05	5.81 ± 0.07	6.11 ± 0.07
Pyrene	5.18	4.44 ± 0.08	4.40 ± 0.02	4.98 ± 0.08	5.22 ± 0.06	5.84 ± 0.07	6.11 ± 0.07
Chrysene	5.61	5.15 ± 0.06	4.86 ± 0.06	5.55 ± 0.07	5.61 ± 0.07	5.69 ± 0.26	6.12 ± 0.08
Benz(a)anthracene	5.91	5.15 ± 0.06	4.86 ± 0.06	5.55 ± 0.07	5.61 ± 0.07	5.69 ± 0.26	6.12 ± 0.08
Benzo(b)fluoranthene	5.8	5.80 ± 0.05	5.17 ± 0.02	5.83 ± 0.10	5.90 ± 0.12	5.79 ± 0.54	6.02 ± 0.11
Benzo(h)fluoranthene	5.8	5.89 ± 0.04	5.23 ± 0.05	5.82 ± 0.11	5.69 ± 0.07	5.85 ± 0.46	6.11 ± 0.14
Benzo[a]pyrene	6.04	5.71 ± 0.14	4.76 ± 0.09	6.30 ± 0.08	6.59 ± 0.11	5.46 ± 0.37	6.25 ± 0.14
Perylene	6.25	5.87 ± 0.09	5.22 ± 0.10	5.87 ± 0.11	5.87 ± 0.08	5.69 ± 0.39	6.05 ± 0.15

**Table 9.** List of experimental log  $K_{PE-W}$  values determined in this study for the priority PAHs and LMW compounds present in the Statfjord crude oil

Compounds	log $k_{ow}$	log $K_{pe-w}$					
		20C @ 0psu	20C @ 35psu	2C @ 0psu	2C @ 100psu	-4C @ 100psu	-15C @ 245psu
Naphthalene	3.37	3.67 ± 0.04	3.62 ± 0.04	3.24 ± 0.08	3.41 ± 0.06	3.56 ± 0.08	3.83 ± 0.22
2-Methyl naphthalene	3.99	3.66 ± 0.08	3.61 ± 0.08	3.26 ± 0.05	3.66 ± 0.08	4.14 ± 0.10	4.48 ± 0.24
Biphenyl	3.9	3.72 ± 0.05	3.76 ± 0.14	3.31 ± 0.04	3.70 ± 0.18	4.29 ± 0.08	4.74 ± 0.23
1,5-Dimethyl naphthalene	4.37	4.17 ± 0.07	4.32 ± 0.06	3.82 ± 0.03	4.29 ± 0.03	4.90 ± 0.09	5.08 ± 0.28
Acenaphthylene	4.2	3.17 ± 0.03	3.36 ± 0.06	2.93 ± 0.05	3.54 ± 0.35	4.28 ± 0.07	4.59 ± 0.15
Acenaphthene	3.92	3.74 ± 0.02	3.95 ± 0.06	3.45 ± 0.05	3.88 ± 0.05	4.40 ± 0.08	4.94 ± 0.22
2,3,5-Trimethyl naphthalene	4.9	4.61 ± 0.05	4.87 ± 0.06	4.25 ± 0.06	4.89 ± 0.04	5.57 ± 0.09	5.38 ± 0.25
Fluorene	4.18	3.75 ± 0.05	4.02 ± 0.05	3.50 ± 0.07	4.07 ± 0.07	4.91 ± 0.09	5.16 ± 0.19
1,4,6,7-Tetramethyl naphthalene	5.3	5.01 ± 0.03	5.30 ± 0.05	4.80 ± 0.06	5.46 ± 0.04	5.98 ± 0.11	5.68 ± 0.29
1,2,5,6-Tetramethyl naphthalene	5.3	4.98 ± 0.02	5.22 ± 0.05	4.87 ± 0.06	5.36 ± 0.05	6.00 ± 0.12	5.79 ± 0.27
Dibenzothiophene	4.38	4.27 ± 0.03	4.44 ± 0.06	4.14 ± 0.04	4.60 ± 0.01	5.42 ± 0.09	5.57 ± 0.24
Phenanthrene	4.46	4.39 ± 0.03	4.62 ± 0.05	4.26 ± 0.06	4.71 ± 0.09	5.45 ± 0.08	5.52 ± 0.26
Anthracene	4.54	4.43 ± 0.03	4.97 ± 0.06	4.30 ± 0.06	4.85 ± 0.09	5.66 ± 0.08	5.59 ± 0.27
1-Methyl phenanthrene	5.14	4.92 ± 0.04	5.17 ± 0.04	5.45 ± 0.08	6.08 ± 0.04	6.14 ± 0.11	5.77 ± 0.27
Fluoranthene	5.22	5.09 ± 0.04	5.30 ± 0.05	4.33 ± 0.07	5.85 ± 0.06	6.11 ± 0.12	5.95 ± 0.27
Pyrene	5.18	5.22 ± 0.05	5.41 ± 0.04	5.30 ± 0.07	5.81 ± 0.04	6.22 ± 0.13	6.09 ± 0.23
Chrysene	5.61	5.91 ± 0.03	6.02 ± 0.04	6.05 ± 0.04	6.43 ± 0.03	6.00 ± 0.17	6.37 ± 0.19
Benz(a)anthracene	5.91	5.91 ± 0.03	6.02 ± 0.04	6.05 ± 0.04	6.43 ± 0.03	5.99 ± 0.17	6.37 ± 0.19
Benzo(b)fluoranthene	5.8	6.36 ± 0.04	6.23 ± 0.04	6.61 ± 0.06	6.37 ± 0.04	5.85 ± 0.14	6.73 ± 0.17
Benzo(h)fluoranthene	5.8	6.56 ± 0.04	6.26 ± 0.02	6.63 ± 0.11	6.41 ± 0.16	5.85 ± 0.23	6.71 ± 0.21
Benzo[a]pyrene	6.04	6.81 ± 0.03	6.60 ± 0.02	6.70 ± 0.05	6.56 ± 0.07	5.83 ± 0.17	7.15 ± 0.22
Perylene	6.25	6.71 ± 0.03	6.60 ± 0.02	6.18 ± 0.06	6.54 ± 0.13	5.97 ± 0.17	6.63 ± 0.17

## 7.0 Achievement and Dissemination

The data gathered to support this study is currently being edited in preparation for submission to *Environmental Science and Technology*.

This data was presented as a platform presentation at SETAC Europe 2009 in Goteborg, Sweden:

Luey, P.; Lohmann, R. *Verification of Polyethylene & Solid Phase Micro-extraction Passive Sampling Devices in Hyper-saline, Arctic conditions*. 19<sup>th</sup> Annual SETAC Europe Meeting, Goteborg, Sweden, June, 2009.

PI Lohmann co-chaired (with Mathijs Smit, *StatoilHydro, TRONDHEIM, Norway*) a session at SETAC Europe 2009 in Goteborg, Sweden, on

- Marine Ecosystems, ME04 - *Polar marine ecotoxicology, risk assessment and monitoring*

This research supported the advancement of Pamela Luey to obtain her Masters of Science degree in Oceanography. She defended her thesis: “Verification of PAH equilibrium partitioning coefficients for polyethylene (PE) sheets & solid phase micro-extraction (SPME) fibers in hyper-saline, Arctic conditions” successfully on December 17, 2009.

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## Appendix



### Coastal Response Research Center

#### CRRC Funded Project Review

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**Project Title: “Detecting dissolved PAHs from oil spills using passive samplers in cold water and ice cores”**

**Principal Investigators: Rainer Lohmann, URI**

#### Reviewer 1

This is an excellent, well written report. This is an extremely detailed report, because it also appears to be a student’s thesis. The end result is a study that is not only applicable to the question of detecting oil-in-ice, but a more broad study that can be used in numerous applications.

**No changes made, as the reviewer appraised our report.**

#### Reviewer 2

The research is definitely good science, but we’re left to wonder what its utility might be in an actual response to an oil spill in ice. It seems to us that determining the concentrations of PAHs could more easily be accomplished by simply taking a sample of the oil and using standard chemical analytical techniques to determine the identity and concentrations of PAHs. This study provides some information of things like routes and concentrations of exposure to PAHs. In that context it might be more useful to Damage Assessment as opposed to response. Nevertheless, it was our assessment that this research had pretty much reached finality. We don’t see the need for significant follow-up research work to answer additional questions. This work has established a technique that could be used to determine PAH concentrations in ice, but it is doubtful to us that such a technique would be heavily utilized. We don’t recommend any additional follow up work.

**No changes made, as the reviewer appraised our work. We agree that damage assessment might be more appropriate then oil spill response.**

#### Reviewer 3

I believe the authors overstate the applicability of their findings. I would suggest that this research is extremely valuable at demonstrating how passive samplers respond in cold water and over a range of salinities, and it demonstrates that passive samplers may be more reliable for estimating concentrations of low molecular weight PAHs when compared to HMW PAH. The polyethylene sheets appear to produce more reliable results than the solid-phase micro-extraction fibers, which also appear to have logistical challenges with their deployment. My conclusion from this research is that passive samplers could be excellent indicators of relative water column oil concentrations--over time, and between locations, but I am not convinced that they can replace analysis of water concentrations or analysis of bivalve tissues as indicators of biological exposure. I have serious concerns regarding our ability to accurately relate passive sampler concentrations to absolute water concentrations. For example, I do not believe they

would be admissible as evidence that water concentrations exceed ambient water quality criteria. But this research does have a lot to offer, and it does not need to be all the things the authors hope.

We appreciate the reviewers overall positive comment on our research, and the detailed suggestions below. We beg to differ that only traditional analysis of water and bivalves are accurate means of representing concentrations and exposure. We assume that passive samplers will increasingly be used to measure time-integrated concentrations in the field.

Specific comments:

There are several places in the text that require some editing. These include page 1, first paragraph, second sentence (suggest changing "these substances" to "oil" since it seems to refer to vessels as substances); second paragraph, third sentence (it is not clear how entrapment in ice sheets cause transport and release, perhaps saying that entrapment, movement, and later melting can extend the toxicity of oil); third paragraph, sixth sentence, delete the first occurrence of "are". Page 4, methods overview, fourth sentence change "equilibrated" to "equilibrate". Page 10, first paragraph, fifth sentence, don't allow the minus sign to become disconnected from the temperature number (- and 15 appear on different lines of text). Page 10, last paragraph, this paragraph is centered rather than left justified. Page 18, first paragraph, first sentence: change "deviations" to "deviation"; and in the last sentence, change SPME to SPMEs. Page 31, last paragraph: change solubility's to solubilities. Page 36, first partial paragraph, the word "higher" is missing from the sixth sentence. Page 43, first full paragraph, change "little HMW" to "few HMW". Page 50, last sentence should read "..were capable of reflecting...". Page 51, conclusions, second sentence, change "increases" to "increase". In the fourth sentence, change to "...reliably demonstrate that the extreme..." Page 50, third paragraph, I suggest "It is suggested that the required deployment time..."

The changes were made, as suggested by the reviewer.

Page 1, third paragraph: It is not clear that passive samplers are preferred to analysis of water or sediment. If what we need to know is the concentration in water or sediment, passive samplers are not preferred.

Whether to use passive samplers or not depends certainly on the goals of a given project and analysis. For example, if sediment concentrations are measured to derive bioaccumulation, it is more straightforward to use passive to measure bioavailability - as documented in several papers. The same logic holds true for water analysis. Basically, passives samplers show a convenient way of measuring what is able to diffuse, and thus what is directly bioavailable, whereas measurements of total (particle-bound + dissolved) concentrations of PAHs in sediment or water do not. This was clarified in the text.

Page 1, third paragraph: PAHs sorbed to particles or colloids are available for uptake by organisms. The mechanism of uptake changes.

The reviewer is partially right, as PAHs on particles can certainly be taken up by organisms, but if they are tightly bound to the particle (such as soot), the PAHs might never be taken up by the organism but excreted again. The text was modified to clarify this point.

The introduction could use additional discussion of what is meant by equilibrium in this context. Later in the paper, the authors seem to suggest that passive samplers can indicate change in concentrations over time. At the beginning, change in concentrations over time are treated as indications of developing equilibrium. Since true equilibrium is difficult to measure, and may be rare in the environment, since concentrations are not static due to currents, ongoing sources, or losses to the atmosphere or to other environmental compartments, it is difficult to know how to interpret concentrations in passive samplers, and even how to verify the relationship between passive sampler and water concentrations appropriately. Some acknowledgement of these challenges would strengthen this paper.

The reviewer is correct, that equilibrium might never been reached in the field. But, it should be pointed out that in reality it is exactly this lack of static concentration that makes passives attractive, as point samplers would be even more in danger of misrepresenting true concentrations over time. The following text was added to clarify this point:

“As stated above, passive samplers take up compounds in proportion to the dissolved concentration present in the environment until equilibrium between the passive sampler and the dissolved concentration is reached. Until equilibrium is reached, the passive samplers reflect a time averaged concentration. If the sampler is deployed longer than needed for equilibrium to be reached, the results will reflect the more recent exposure. Conventional methods of water analysis take samples at a discrete point in time, representing the concentration only at that time. Depending on the circumstances of the sample collection, such as currents, changing tides, losses to the atmosphere, or other environmental factors, the discrete sample is not an accurate representation of the overall concentrations in the environment. The time averaged concentration determined from passive sampling is a more appropriate reflection of the longer-term exposure in the environment.”

“Equilibrium is defined as the distribution of a chemical in two phases as governed by the free energy for this process. At equilibrium, no net change in concentration between the phases occurs over time. Equilibrium partitioning coefficients are used to represent this relationship.”

Page 10: It would help if the difference between the two sources of salt could be compared using (otherwise) the same attributes to document that the source of the salt had no effect on results. It is unclear what effect stirring and shaking had on results. Shaking was intended to speed equilibrium, but it is not clear how well it mimics conditions in the field. Comparing results between shaken and unshaken conditions might be interesting. Explain why devices were wiped with a kimwipe, and what effect that might have had compared to allowing the devices to air dry.

This was clarified, as suggested by the reviewer, in the following text:

“To ensure modifying the salt would not affect the results, the composition of the two salt mixtures was compared. Manufacturer tables describing the compositions showed the only difference between the mixtures were in the ancillary ingredients, not the major components in the mixtures.”

“These conditions would mimic a very turbulent situation in the natural environment. If the samplers were not agitated in this method, it would take a much longer time period to reach equilibrium.”

“wiped dry with a Kimwipe<sup>®</sup> (to avoid contamination)”

Page 13, second paragraph: It would help to explain why the copper housing was needed to house the SPMEs. The effect this housing has on water circulation and the time to reach "equilibrium" could be discussed.

This was explained, as suggested by the reviewer, in the following text:

“The delicate nature of the SPME fibers necessitated some sort of housing to be utilized for the deployment. The housing enabled the SPMEs to be attached to the deployment line in the same fashion as the PEs, facilitating the comparison of the samplers, as well as protected them from the environment. The concentration of PRCs remaining in the samplers after the deployment was confirmed to assess if adequate water circulation occurred during the deployment.”

Page 13, third paragraph, last sentence: I believe the water concentrations were derived using equation 2, not equation 3.

The changes were made, as suggested by the reviewer.

Page 20, figure 9: 100% concentration does not have any variance. What concentration was used as 100% (average of replicates?)

Figure 9 represents the loss of PRCs. 100% lost means that the PRCs were all lost - in other words, equilibrium was reached for that compound.

Page 21, last paragraph: It is not clear what is meant by "complications of the compounds".

This was briefly clarified in the text.

Page 23, second full paragraph: Excluding samples that vary is not a satisfying approach. Do the authors have any thoughts about why SPMEs have more problems than the PEs?

This was briefly clarified in the text. It is thought SPMEs have a higher degree of sensitivity due to their thinner film available for accumulation by contaminants.

Page 24, first partial paragraph, last sentence: I think this needs more explanation. It is not immediately obvious how the plots validate the passive samplers and extraction methods.

The changes were made, as suggested by the reviewer, in the following text:

“Since the theoretical values were taken from peer-reviewed studies, the agreement between experimental and theoretical values validates the passive samplers and extraction methods used in this study.”

Page 31, second full paragraph: How is it that the outlying results of two SPME samples are due to sampling error?

This was briefly clarified in the text.

Page 36, first paragraph: Are there other explanations for the anthracene data outliers for the SPMEs?

We checked the raw data, and have no explanation for the outliers. The following was also added to the text:

“The data was rechecked to ensure it was properly captured, however there was no explanation for this difference.”

Page 43, first partial paragraph: The ability of compounds to dissolve more readily into water does NOT make them more acutely toxic. It might make them more available.

This was briefly clarified in the text.

Page 43, third full paragraph: Either explain Bradsted's concern more fully, or delete this paragraph. It is not clear why he would be concerned that biological action would continue even after the samples were treated with biocide.

This was explained, as suggested by the reviewer, in the following text:

“After discussion with colleagues, it was discovered that even though the water was treated with biocide there was potential over longer term experiments for bacteria to re-grow after the initial biocide treatment and potentially biodegrade the PAHs changing the composition of the WSF sample (Odd Gunnar Bradsted, SINTEF, personal communication). To ensure that there was no bacterial degradation of oil during the experiment, two time periods were selected, three and four weeks, for comparison of concentrations over time.”

Page 43, fourth full paragraph: Predicting water samples within a factor of two does not allow passive samplers to replace analysis of water samples, though this depends on the purpose of the sampling.

This was explained, as suggested by the reviewer, in the following text:

“Since concentrations in the natural environment are not static due to factors such as currents, changing tides, losses to the atmosphere, etc., a snapshot sample taken cannot be representative of passive sampler exposure. Additionally, conventional extraction methods of total water concentrations by definition will tend to over-estimate the dissolved concentration in the environment. Thus, we consider an agreement within a factor of two between passive samplers and conventional methods to be an acceptable standard. This agreement demonstrates passive samplers can be a valuable tool in oil spill monitoring and damage assessments.”

Page 43, fifth paragraph: If naphthalene was volatilizing from the samples, was equilibrium possible within the time frame tested? How could samples have been contaminated during extraction?

This was briefly clarified in the text.

Page 46, first paragraph: Do quality assurance samples provide any indication of whether liquid-liquid extraction could not recover the fluorene? Again, what does "complications with the methylated compounds" refer to?

This was explained, as suggested by the reviewer, in the following text:

“The underestimation of the methyl-fluorene and –phenanthrene by the passive samplers implies there could be complications in assessing equilibrium concentrations for the methylated compounds. Perhaps using a methylated PRC for this investigation could have better represented the kinetics of the methylated compounds in the passive samplers.”

Page 50, third paragraph: The discussion of the change in water concentrations over time and related changes in passive sampler concentrations seems to suggest that passive samplers should be able to track changing water concentrations over time. But on page 18, it seems to take three weeks for samplers to reach equilibrium.

The changes were made, as suggested by the reviewer, in the following text:

“From previous work we know that PE samplers equilibrate for the lower molecular weight PAHs (such as acenaphthene and fluorene) in a matter of several days in Narragansett Bay. Thus, changes in the accumulation of these PAHs in passive samplers over time likely reflects increasing dissolved concentrations. In contrast, the higher molecular weight compounds, with their increased equilibrium time, would not have sufficient time to reflect this increase.”

Conclusions: It would be useful to pull several additional considerations into the conclusions. The samplers do not accumulate phenols. It is not clear how samplers could evaluate extremes or average concentrations over time. Higher log Kow compounds did not reach equilibrium, and their concentrations may not be accurately predicted. The possibility that field blanks may have higher PAH concentrations than samplers after deployment is disturbing. Do the authors have thoughts about how to address this problem?

The changes were made, as suggested by the reviewer, in the following text:

“This study commenced to examine the effect of temperature and salinity on the equilibrium partitioning coefficients of passive samplers, so they may be an effective tool at investigating the fate and transport of oil, specifically PAHs, in the Arctic environment. Time constraints linked to the simultaneous analysis of phenols and PAHs by GC-MS prevented us from studying the uptake of phenols by passive samplers. We note, however, that other studies have shown passives samplers, such as PE, are capable to reliably predict water concentrations of polar compounds (e.g., Sacks, 2010). For the PAHs investigated, it was expected the equilibrium partitioning coefficients would increase with decreasing temperature and increasing salinity. The combination of the decreasing temperature and increasing salinity is substantial in the Arctic environment and possesses a potential complication when utilizing passive samplers. This study was able to reliably demonstrate that the extreme temperature and salinity conditions that passive samplers would face in the Arctic environment do have a significant effect on the partitioning of compounds into passive samplers. Both temperature and salinity must be accounted for when deploying passive samplers in this unique environment (Tables 8 & 9). Another effect of this harsh environment when deploying passive samplers is allowing sufficient time for the passive samplers to reach equilibrium, especially for the higher molecular weight compounds. PRCs can be employed to reflect equilibrium concentrations; however, a more diverse mixture of PRCs maybe needed in the Arctic environment to address the equilibrium time of the higher molecular weight compounds and the methylated compounds. Through the crude oil study, as well as the field

deployment, these passive samplers have revealed they are able to be deployed either during an oil spill event or prior an oil spill to study background concentrations and can accurately reflect the PAH concentrations present in the water column. The PE passive samplers were able to avoid complications in experiments and with their larger volume can more readily be deployed to determine background concentrations. The SPMEs and PEs can be deployed to represent time averaged concentrations, representing more accurate environmental concentrations, averaging out incorrect extreme concentrations that could be captured with discrete sampling. Because of this unique time averaged sampling, they may be useful to determine concentrations after an oil spill event. They are a valuable resource in studying the fate and transport of oil in ice, and with the completion of this study are now able to be used reliably.”